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CLINICAL CHEMISTRY

BY

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SEVENTH EDITION—REVISED

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PREFACE TO SEVENTH EDITION

"It has been said that Alexander Pope is a poet whom everybody quotes and nobody reads. It may be said of Compends that they are books that most professors and reviewers condemn and nearly all students use. The truth is, that in the present systems in professional schools, students are obliged to meet two distinct requirements. They must study for the knowledge necessary for the practice of the profession and they must study to pass examinations. The latter are in so many cases arbitrary in scope, and affected by the personal equation of the examiner, that the student cannot be blamed for resorting to a concise presentation of the more important facts of the science, supplementing this by notes of the narrower and more strictly personal items of the teaching. Some teachers hold that note-taking is the best method, and are opposed to printed summaries because these latter obviate the student's obligation to take notes. In a large experience with a class of students of the best type of those in American professional schools, I have been led to the view that voluminous note-taking is not a good method. The pronunciation of technical terms is so irregular, and many of them are so strange to students, that they are entered erroneously in the notes and serious errors may be made and persist. The written word is necessary to full knowledge; the compend affords this aid. Modern chemistry is so extensive in its range and variety of facts and so highly specialized in its practical applications that careful selection is necessary, and this selection must be made with reference to the students for whom the work is intended."

The above paragraph is quoted from the previous edition of this work, as it expresses facts now as well as it did then.

Since the last edition of this work great changes have taken place in chemistry, not only in the enormous increase of data, but in the upsetting of some long established theories. Indivisibility of the atom and independence of each element were prominent features in the science throughout most of the nineteenth century, but both views have been abandoned. The newer theories are still not fully developed and, therefore, need only

brief allusion. A notable change that has attended the researches into atomic and molecular structure is the development of physical chemistry, which is progressing to such extent as to threaten the existence of chemistry as a distinct science. However, a work like the present deals almost entirely with the applications of the science, and hence needs less attention to the abstruse phases of it. Notice has been made in the revision of the more important advances. The extensive researches into radioactivity and the phenomena of atomic disintegration as shown in the transformation of uranium into radium and this in turn into a series of products have been the cause of great modification of our views of the nature of matter.

Some of the most important developments in applied chemistry are in connection with biology, especially in procedures for diagnosis and prognosis, comprehended under the title "Clinical Chemistry." Much addition has been made to this portion of the book. Mr. Trumper's large experience in clinical chemistry both in private laboratory practise and in the Jefferson Hospital has been utilized in the thorough revision of the sections on Gastric Contents, Milk and Urine, and he has added a comprehensive section on Blood Chemistry.

The authors are under obligation to Messrs. P. Blakiston's Son & Co. for permission to use material from Leffmann and LaWall's "Organic Chemistry," Hawk's "Physiological Chemistry" and Stitt's "Practical Bacteriology."

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INORGANIC CHEMISTRY

PRINCIPLES

GENERAL PRINCIPLES

Chemistry is the science that investigates the composition of matter.

Matter is anything that occupies space and has weight.

Changes may be distinguished as *physical* or *chemical*. *Physical change* is in general that which occurs without change of composition. The development of magnetic properties in iron is an example of a physical change. The most frequent instances of true physical change are those known as *changes of state*. Matter is considered to exist in at least three states—*solid*, *liquid*, and *gaseous*. The change from one of these conditions to the other takes place under the influence of temperature, and is not necessarily attended by any alteration of composition. Such is the case in the conversion of ice into water, or water into steam, or the reverse. In many cases the conversion of a solid into a liquid, or of a liquid into a gas, is attended by change of composition, and, therefore, is not merely a physical change. *Chemical change*, the proper study of chemistry, is that attended by alteration of composition. The rusting of iron, burning of coal, rotting of animal and vegetable matter are familiar instances of chemical change.

Forms of Chemical Change.—These are combination, decomposition, and re-arrangement. *Combination* is the association of substance to form a new substance; *decomposition* is separation into new substances. *Rearrangement* refers to cases in which new substances are formed without combination or decomposition.

Atom and Element.—These terms, very important in chemistry, have suffered much change in meaning of late years. Nearly twenty-five centuries ago some Greek philosophers propounded the view that all matter is made up of minute, indivisible particles. They coined from their

own language the adjective "atomos" (indivisible), for such particles. Their views received but little attention and for many centuries were without appreciable influence upon thought and experiment. In the early part of the nineteenth century, John Dalton, a British scientist, applied the theory in such form that it became generally adopted by chemists and physicists. The particles, termed "atoms" were considered to be extremely minute and wholly inalterable either chemically or physically. There was also developed the view that all matter is made up of a limited number of distinct substances not convertible into each other. These were termed "elements." By association of two or more elements compounds are formed. This view is also ancient in its simpler form, as it is clearly set forth in a Latin poem by Lucretius an Epicurian philosopher of the first century of the present era.

In the progress of science since the beginning of the present century both these views have been abandoned. The atom is now regarded as made up of electrical charges, a nucleus (proton) having a positive charge, constituting almost the whole mass of the atom and one or more negative charges (electrons) which are but a minute proportion of the mass. The electrons balance the positive charge of the nucleus and the atom in its normal state is without electrical manifestation. The number of electrons depends on the atomic weight. Hydrogen which has the lowest atomic weight has one, uranium which has the highest atomic weight has ninety-two.

Notwithstanding these radical changes in the atomic theory, the atom as a mass is the unit of chemical action, and in elementary chemistry may be considered as such. It is, however, known that with many elements the atoms are not all alike (for the same element) but differ slightly in weight due to differences in the nucleus. These are too slight to make a difference in the position of the element in the periodic table (see page 38) hence they are called "isotopes" a term from the Greek meaning "same place." Some elements have been found to have as many as seven isotopes. No account is yet being taken of these complex conditions in the ordinary operations of chemistry. In a few instances isotopes of different elements have the same weight. Such coincidences are termed "isobars," that is, "same weight." The progress of research has developed some general principles.

1st. That the atom of each element has definite weight within narrow limits.

2d. That the atom of hydrogen is the lightest of all.

3d. That combination takes place among atoms under the action of chemical affinity, forming "molecules."

Starting with the first two principles numbers have been obtained which are supposed to represent the weight of each atom compared to the atom of hydrogen. These numbers are called ATOMIC WEIGHTS.

In any compound the sum of all the atomic weights is called the *molecular* weight. Thus, sulphuric acid is H_2SO_4; its molecular weight is 98.

$$\begin{aligned} H_2 &= 2\ (2 \times 1) \\ S &= 32 \\ O_4 &= 64\ (16 \times 4) \\ &\overline{98} \end{aligned}$$

Hydrogen and Oxygen Standards for Atomic Weight.—In the original determinations of atomic weights the numbers 1 and 16 were assigned, respectively, to hydrogen and oxygen, but later researches have shown that this is not the exact ratio. At present, it is regarded as about 1 to 15.88. Hence, two systems of calculating atomic weights have arisen. In that adopted in this book, oxygen is taken as 16; this makes hydrogen, approximately, 1.008, but the decimal is usually disregarded. In the other system, oxygen is 15.88 and hydrogen is 1. As the whole arrangement is one of relative and not absolute weights, it is not a matter of great importance which system is used, but all atomic weights used in calculation should be on one or the other system and the basis O = 16 is now used.

Nearly one hundred elements are now known. A list with symbols and atomic weights is given on page 101.

NOTATION

In chemistry, a *symbol* is an abbreviation of the name of an element; in most cases an initial letter is used, as C for carbon, P for phosphorus. Since some elements have names beginning with the same letter, proper distinction is obtained by assigning the single letter to the most common, and attaching small letters to the other initials. Thus C stands for carbon, Ca for calcium, Cl for chlorine Cd for cadmium. Some elements have different names in different languages, and for these the symbol is formed from the Latin name. Iron, for instance, is represented by Fe (*ferrum*); lead by Pb (*plumbum*); silver by Ag (*argentum*); potassium by K (*kalium*).

To express combination between elements—in other words, to express the composition of a compound body or of a molecule—the symbols are

to be written together like the letters of a word. Such a collection of symbols is called a FORMULA.

The symbol, however, not only represents the element, but one atom of it. The expression CaO not only shows a compound consisting of calcium and oxygen, but also indicates that it contains a single atom of each element. CaO_2 shows that two atoms of oxygen are present and one of calcium. In writing these expressions certain rules are followed:—

1st. To multiply an atom, a small number is attached to the lower right hand, as seen above, where O_2 indicates two of oxygen. The formula $C_2H_4O_2$ shows a combination consisting of two atoms of carbon, four of hydrogen and two of oxygen.

2d. To multiply several atoms by the same number, a large figure is placed in front. Thus $2HClO$ is equal to $H_2Cl_2O_2$; that is, the large figure multiplies the whole expression.

3d. To multiply a portion of an expression, several methods are in use. The part to be multiplied may be placed in parentheses, and the proper number attached to the right-hand corner. $Ba(NO_3)_2$, for instance, equals BaN_2O_6; $C_6H_8(NO_2)_2O_5$ equals $C_6H_8N_2O_9$. The effect of the small figure is limited to the part within the parentheses. This method is especially adapted to multiplying symbols in the middle or at the end of a formula. To multiply the symbols at the beginning of a formula, it is usual to point off or punctuate the part to be affected, and place a large figure in front. Some irregularity prevails as to the particular sign used, the comma and semicolon both being employed. It is sufficient for the student to bear in mind that a punctuation mark or arithmetical sign in a formula will stop the multiplying effect of the large figure at the beginning of the expression. For instance, $2C_2H_5$, H_2N is equal to $C_4H_{10}H_2N$; similarly, in $2FeSO_4 + HCl$ the letters following the plus sign are not affected by the figure 2. If it is desired to carry the multiplying effect to the end of the expression, it is enclosed in parentheses; thus, $2(FeSO_4 + HCl)$. Here all the letters are equally influenced.

Since the symbol of each element represents one atom, it follows that every symbol carries with it an idea of quantity. HCl means not merely that hydrogen and chlorine are in combination but that the amounts by weight are in the proportion of the atomic weights; *i. e.*, 1 (atomic weight H) to 35.46 (atomic weight Cl). When the symbol is multiplied, the weight is also multiplied. For instance, H_2O represents 2 parts by weight of H to 16 of O; $HgCl_2$ represents 200.6 parts of mercury and 70.92 (35.46×2) parts of chlorine.

Empirical, Rational and Structural Formulas.—When symbols are written so as to show merely the total number of each of the atoms present, the formula is termed *empirical.* When some arrangement of the atoms is indicated the formula is termed *rational.* A *structural* formula is one that is intended to show the supposed relative positions of atoms in space. H_3PO_2 is the empirical formula of hypophosphorous acid; $(HO)H_2PO$ is the rational formula. For structural formulas, see page 13.

Stereochemic Formulas.—All molecules, being composed of atoms, which are particles of matter, occupy space and, therefore, have the three dimensions of length, breadth and thickness, which are the inherent properties of all matter. Hence the formula of any substance can only be completely shown by use of these three dimensions. Formulas constructed on this plan are called *stereochemic formulas.* For illustrations, see under "Organic Chemistry."

NOMENCLATURE

The names of chemical compounds are regulated by a system which depends largely on the employment of terminations.

In the old division of the elements into metals and non-metals, the metals were usually distinguished by the termination "*um.*" A change of this termination into "*a*" indicated combination with oxygen. Potassium (K) becomes by oxidation potassa (K_2O); sodium (Na) becomes soda (Na_2O); magnesium (Mg) becomes magnesia (MgO). As the names of many of the common metals do not end in "um" unless the Latin name is used, this rule is only of limited application.

Chemical compounds which contain only two elements are called *binary compounds.* They are usually named by joining the names of the elements present and attaching to one of them the termination "*ide.*" This termination may be conveniently regarded as an equivalent of the phrase "nothing else;" that is, wherever it occurs it indicates that nothing else is present except what is expressly mentioned. Potassium iodide for instance, can contain nothing else but potassium and iodine; copper sulphide can contain nothing but copper and sulphur.

PbO..... Lead ox*ide.*
NaCl..... Sodium chlor*ide.*
AgBr..... Silver brom*ide.*

The syllable "ide" is usually attached to the members of the oxygen, chlorine, nitrogen and carbon groups, and preferably to those of the first

two groups. Thus, a compound of iron and carbon is called iron carbide but a compound of carbon and chlorine is called carbon chloride.

In many books, especially in older works, the word "of" will be found frequently used in the names of compounds. Instead of copper nitrate, we see nitrate of copper, for potassium iodide, iodide of potassium. This is not regarded as proper form.

As elements may combine in several proportions, forming several different compounds, this termination "ide" does not suffice. The bodies Cu_2O and CuO are both properly called copper oxide, because they contain only copper and oxygen, but are different bodies. In the same way, SO_2 and SO_3 are both sulphur oxide. The distinction is made by prefixes,

Cu_2O	Copper *sub*oxide.
CuO	" *mon*oxide.
SO_2	Sulphur *di*oxide.
SO_3	" *tri*oxide (also *ter*oxide).
CCl_4	Carbon *tetra*chloride.
PCl_5	Phosphorus *penta*chloride.

Sub generally indicates deficiency; that is, that the quantity of the element to which it is attached is less than it should be. The term *sub* is applied especially to compounds in which a member of the oxygen or chlorine group is deficient in amount. Pb_2Cl, Zn_3I_2, Cu_4O would be sub-compounds.

Some elements form compounds in which the proportion is as 1 to $1\frac{1}{2}$, but as fractions are not allowed in formulas, the whole expression is multiplied by 2, which gives the proportion 2 to 3. $FeO1\frac{1}{2}$ becomes, therefore, Fe_2O_3. These are called *sesqui*-compounds. Fe_2O_3 is iron sesquioxide. The word *sesqui* means one and a half, and conveys the idea that the relation between the two elements is as 1 to $1\frac{1}{2}$ to (2 to 3).

In the case of few binary compounds, especially when they are obviously supersaturated (see p. 11), the term "*per*" is employed in preference to syllables indicating number. Thus H_2O_2 is called hydrogen *peroxide* rather than hydrogen *dioxide*.

There is no uniform method for giving names to compounds containing more than two elements. Sometimes the system is the same as that just given; all the elements are mentioned and the termination "ide" is attached. Thus KHO is potassium hydroxide NaHO is sodium hydroxide. In other cases a portion of the compound is included under a group name, and this is joined with the names of the other elements according to the

above rule. Thus KCN is not called potassium carbonitride but CN is called cyanogen, and the entire compound is called potassium cyanide.

Among the compounds containing three elements are those which are called *salts*. If zinc is placed in sulphuric acid, a zinc salt is formed, zinc sulphate; also by direct union of many oxides; for instance, when calcium oxide, CaO, acts with carbon dioxide CO_2, we get calcium carbonate, $CaCO_3$, a *salt*.

Most salts contain *three* elements, of which *oxygen* is one, and the names are made by joining the names of the other two elements and adding to them certain syllables which not only indicate the presence of oxygen, but also partly the amount. These syllables are *ate* and *ite*. The former indicates the greater quantity of oxygen. The potassium sulph*ate* and potassium sulph*ite* both contain oxygen, but the former (sulph*ate*) contains the more oxygen. Sodium nitr*ate* and sodium nitr*ite* contain the same elements, but their composition is $NaNO_3$ and $NaNO_2$. respectively.

It has been pointed out that the syllable "ide" can be regarded as equivalent to the phrase "nothing else." In the same manner, the syllables *ate* and *ite* may be regarded as meaning "something else," generally oxygen. Thus, while in sodium sulph*ide* but two elements are present, sodium sulph*ate* and sulph*ite* will contain three.

These two terminations are not sufficient. Potassium, chlorine and oxygen unite in four different proportions, forming $KClO_4$, $KClO_3$, $KClO_2$, KClO. In such cases the important or most common compound is distinguished by the termination *ate*, and the one containing the next lower amount of oxygen by the termination *ite*.

The other compounds are indicated by the use of certain extra syllables, *hypo* and *hyper*, the latter now generally abbreviated to "per." The significance and use of these syllables are shown in the following table:

$KClO_4$	Potassium	perchlorate.
$KClO_3$	"	chlorate.
$KClO_2$	"	chlorite.
KClO	"	hypochlorite.
Na_2SO_4	Sodium	sulphate.
Na_2SO_3	"	sulphite.
Na_2SO_2	"	hyposulphite.

(Note: This "hyposulphite" is not the substance used as a fixing agent in photography. That is $Na_2S_2O_3$ and its proper name is "sodium thiosulphate.")

When hydrogen is present in such compounds, a different method is adopted.

Thus $HClO_4$, $HClO_3$, $HClO_2$, HClO are known; these might be called hydrogen perchlorate, hydrogen chlorate, etc. The usual method is to drop the word hydrogen, change the termination *ate* into *ic*, the termination *ite* into *ous*, and add the word acid,

$HClO_4$	Perchlor*ic* acid.
$HClO_3$	Chlor*ic* acid.
$HClO_2$	Chloro*us* acid.
HClO	Hypochloro*us* acid.

The *prefixes* are retained without change, and the syllable *ic* corresponds to *ate*, and the syllable *ous* to *ite*.

Potassium sulphate K_2SO_4	corresponds to	Sulphuric acid H_2SO_4
Potassium sulphite K_2SO_3	"	Sulphurous acid H_2SO_3
Potassium hyposulphate K_2SO_2	"	Hyposulphurous acid H_2SO_2

Sometimes the hydrogen is only partly replaced by another element, and the body is intermediate between the acids and the salts. Thus $KHSO_4$ is at once a potassium and a hydrogen compound. It is called acid potassium sulphate or potassium hydrogen sulphate. The word *acid* calls attention to the hydrogen. These acid salts are not infrequently called *bi*-salts. Acid potassium sulphate is known in commerce as potassium bisulphate; the corresponding acid carbonate, $KHCO_3$, as bicarbonate. "*bi*" is also used in a few cases in which "di" is now preferred.

The terminations "ous" and "ic" are employed with elements forming two sets of compounds.

Iron forms two chlorides, two iodides, two sulphides, etc., as follows:

FeO	$FeCl_2$	$FeSO_4$	Ferro*us* salts.
Fe_2O_3	$FeCl_3$	$Fe_2(SO_4)_3$	Ferr*ic* "

These terminations do not indicate the amount of the element to which they are attached, but of the other substances; *ous*, as usual, means less than *ic*.

LAWS OF COMBINATION

The great law of chemistry is the law of *constant proportion. Every chemical compound is definite in its nature, the proportion of its constituents*

being constant. Water, for instance, when pure, always consists of 11.2 of hydrogen and 88.8 % of oxygen.

Elements, however, are not limited to one proportion of combination, but in each proportion a different body is produced. Thus, there is a compound containing about 6 % of hydrogen and 94 % of oxygen. It is, however, very different from water. So, also, there are five compounds of nitrogen and oxygen, all different bodies. When the proportions present in different compounds are expressed in terms of atomic weight, it is generally found that a simple multiple relation exists. For instance, the two compounds of hydrogen and oxygen have the formula, respectively,

H_2O..... Water.
H_2O_2..... Hydrogen dioxide (peroxide).

The five compounds of nitrogen and oxygen are N_2O, NO, N_2O_3, NO_2, N_2O_5.

The fact has given rise to a second law, or rather rule, called the *law of multiple proportion. When elements combine in more than one proportion, the higher proportions are simple multiples of the lower.*

The same simplicity and constancy of proportion is observed in the combination of compound bodies. The combining weight of a compound body equals the sum of the atomic weights of its constituents. Thus, lime (calcium oxide), CaO, has the combining weight—

$$\begin{aligned} Ca &= 40 \\ O &= 16 \\ \hline CaO &= 56 \end{aligned}$$

When lime and water are mixed they combine in definite proportions of their molecular weight—

$$\begin{aligned} H_2 &= 2 \\ O &= 16 \\ \hline H_2O &= 18 \end{aligned}$$

56.0 parts by weight of lime with 18 parts by weight of water, forming 74.0 parts of slacked lime—

$$CaO + H_2O \rightarrow CaH_2O_2.$$

VALENCY

Elements, as noted, may combine in several proportions. When compounds containing the same elements are compared, there is usually one proportion which seems to be the most natural; it is either most frequently or easily produced, or it is the one least liable to change. Hydrogen and oxygen combine in two proportions, thus:

2 parts by weight H, 16 " " " O } = H_2O. Hydrogen monoxide.

2 parts by weight H, 32 " " " O } = H_2O_2. Hydrogen dioxide (peroxide).

These bodies are very different. The first is *water*, a compound not liable to decompose. The second substance is difficult to prepare and to preserve; it is liable to explode. It may be assumed, therefore, that the normal proportion of combination between H and O is H_2O. Carbon forms with oxygen two well marked compounds, CO and CO_2. CO is formed when carbon is burned in a *deficient* supply of oxygen, but CO_2 is formed when the carbon burns under natural conditions in a free draft of air or oxygen. CO, besides, shows a tendency to take up more oxygen, especially when heated, and it will combine with chlorine, even at ordinary temperatures. CO_2, on the other hand, shows no tendency to combine with either oxygen or chlorine.

The atom of hydrogen is taken as a point of comparison, and each element compared according to the number of hydrogen atoms with which it forms the most permanent combination. For instance:

Cl	combines with	H,	forming	HCl.
Br	"	"	H,	"	HBr.
O	"	"	H_2,	"	H_2O.
S	"	"	H_2,	"	H_2S.
N	"	"	H_3,	"	H_3N.
As	"	"	H_3,	"	H_3As.
C	"	"	H_4,	"	H_4C.

These are not the only compounds that can be formed from these elements, but they are those which show only a slight tendency either to take new atoms or give up what they already possess.

The number of hydrogen atoms with which any element combines is called its VALENCY. Degrees of valency are indicated by names and

Roman numerals, the latter being placed to the upper right hand of the symbol.

I	indicates	a monad (monatomic or monovalent).
II	"	a dyad (diatomic or bivalent).
III	"	a triad (triatomic or trivalent).
IV	"	a tetrad (tetratomic or tetravalent).
V	"	a pentad (pentatomic or pentivalent).
VI	"	a hexad (hexatomic or hexivalent).
VII	"	a heptad (heptatomic or heptivalent).

Valency has nothing to do with the energy or activity of the element. It is a measure of capacity only. Bodies of high valency are often of weak affinity, while some of the strongest chemical agents are of low valency. Chlorine has ordinarily only one-third the valency of nitrogen, but it is much more active in the free state.

Degrees of valency are determined by a study of the proportions in which bodies combine; a knowledge of the valency of the elements is a key to the composition of all their important and more permanent compounds. The following gives the valency of some of the groups of elements:—

Monad,—potassium and chlorine groups.

Dyad,—oxygen, iron, calcium, zinc groups, and frequently the iron group.

Triad and pentad,—nitrogen group.

Tetrad,—carbon group and sometimes the iron group.

When elements are combined in such proportions that their valencies are equalized, the compounds are said to be *saturated*. This meaning must be distinguished from the more common one, viz., that a body has dissolved or absorbed as much of any substance as it can take up. A *saturated solution* is a solution which contains as much of any substance as can be dissolved.

Taking the monad group, for instance, the members being equal to one atom of H, they are equal to each other. Hence, K and Cl will combine in equal number of atoms, forming KCl, potassium chloride NaBr, AgI, LiCl are other examples. The dyad elements have twice the combining capacity of monads; therefore, the compound of sodium and oxygen will be Na_2O.

The combination between triad antimony and monad chlorine will be $SbCl_3$; between tetrad carbon and dyad oxygen, CO_2; between pentad nitrogen and dyad oxygen, N_2O_5.

The degrees of valency given above are not invariable. The circumstances under which the variation takes place cannot be very well defined; but the extent or rate of variation is by a simple law, to which only a few exceptions need be made. *When an element changes its valency, either increasing or diminishing, the change is by two degrees at a time.* Elements of even valency remain even, passing, for instance, from hexads to tetrads, and finally to dyads, or the reverse; elements of uneven valency remain uneven, passing from pentads to triads and monads, and the reverse. It has been suggested that variation in valency is due to change in the number or arrangement of electrons.

Some elements seem to be exceptional, but, by a supposition, the application of the law is retained. These bodies are supposed to have the property of combining with themselves in such a manner as to form double atoms, possessing a valency greater than either atom singly, but less than the sum of the valencies of the two atoms. Iron, generally a dyad, becomes in certain compounds a tetrad, but two atoms of iron are supposed to unite and form a double atom, which then forms compounds with other elements. Obviously, this double atom, formed from two atoms each having a capacity of four, will have a power of six, one degree of valency in each atom being rendered *latent*. See next page, under "Graphic Formulas."

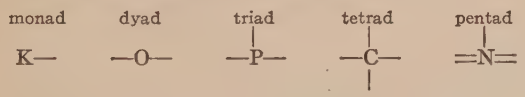
To distinguish varying valency, the terminations *ous* and *ic* are employed, *ous* indicating the lower degree and *ic* the higher. Thus, manganous (lower valency) and manganic (higher valency) salts are indicated, ferrous (dyad) and ferric (hexad) compounds. In the terminations of the names of acids the same principle is carried out, sulphurous acid being the compound in which sulphur has a lower (tetrad) valency; sulphuric acid one in which sulphur has a higher (hexad) power.

Valency is utilized for determining the proportion of combinations between any two elements, and starting with the formula of any compound, it is possible to obtain, by substitution, the formula of any derivative. Thus, nitric acid forms derivatives, called nitrates, in which the hydrogen of the acid is replaced by other positives. Suppose the formula of potassium nitrate is desired, the reasoning would be as follows: Nitric acid is HNO_3, potassium is a monad; one atom of potassium will substitute the atom of hydrogen, and the formula is KNO_3. By the same reasoning the formula of copper sulphate may be deduced. Sulphuric acid is H_2SO_4, copper is a dyad; one atom of copper will displace two of hydrogen; therefore, $CuSO_4$. When the standard formula contains too small an

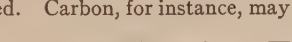
amount of hydrogen, we must multiply the expression by some whole number. For instance, the formula of copper nitrate will be deduced in this manner: Nitric acid is HNO_3, copper is a dyad; copper will therefore replace the hydrogen of two molecules of nitric acid; hence, $Cu(NO_3)_2$.

If one or more atoms are taken from a saturated compound, the compound is unsaturated to a degree equal to the hydrogen atoms to which the removed atoms correspond. The group H_4C is saturated. The group H_3C can take up one H or its equivalent, and is therefore a monad; H_2C can take up H_2, and is therefore a dyad; and so on. The valency of any molecule can thus be obtained by finding how much hydrogen is required to form a saturated compound. By this method it is seen that HO is a monad, for it requires but one atom of H to complete the molecule; CO_3 is a dyad, for it requires H_2 to form the saturated compound H_2CO_3; PO_4 is a triad, for it forms H_3PO_4. (See section on Radicals.)

Structural (Graphic) Formula.—This is a convenient and much used method of indicating valencies. It consists of the symbols with bonds or prolongations the same in number as the degrees of valency. Taking some common elements as examples, the forms are

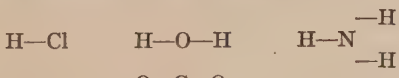


These bonds may be attached in any position or direction as long as the proper number is used. Carbon, for instance, may be written as above, or



or in any other way, provided four bonds are present.

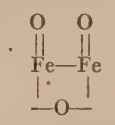
In the practical application of this notation the bonds of the different elements are linked and when all the points are joined the compound is complete, and is a saturated molecule. Two bonds of one atom must not be attached to one bond of another atom. The following are examples of some common compounds written graphically:—

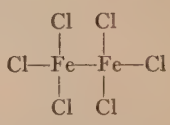


Unsaturated molecules may be indicated. Thus, O=C= shows that carbon monoxide is a body having two degrees of valency unsatisfied;

$O{=}C{=}\begin{matrix}Cl\\Cl\end{matrix}$ that two atoms of chlorine have combined and satisfied this free valency.

The nature of the change by which the iron atom passes from a dyad to a hexad condition can be very well shown by this method. Dyad iron, graphically represented, would be Fe=, in which two bonds have disappeared, leaving two still active. In the higher degree of valency (tetrad), the condition is $-\overset{|}{\underset{|}{Fe}}-\overset{|}{\underset{|}{Fe}}-$; one bond of each atom is latent and links the two in chemical union. Ferric oxide and ferric chloride would be





ELECTRICAL RELATIONS OF THE ELEMENTS

Electrical excitement exhibits two conditions, called respectively *positive* and *negative*, produced in any apparatus developing electricity, The points at which the electrical excitement is manifested—for instance. the ends of the wires from a battery or dynamo—are called *poles*. The positive pole, often called the *anode*, is distinguished by the sign +, and the negative, often called the *kathode*, by the sign −.

Two bodies differently electrified will attract each other, but if charged with the same kind of electricity will repel. The law is generally expressed as follows: *Like electricities repel; unlike attract.*

These principles have been applied to the determination of some important relations between elements. A current of electricity decomposes many substances, some elements appearing at the positive pole, and others at the negative. Thus, potassium will be liberated at the negative pole (kathode), and oxygen at the positive (anode). This will be the invariable result with these elements, no matter what compounds be taken for the experiment, but with many other elements the result will depend upon the compound.

Since unlike electricities attract, it follows that elements which go to the positive side must be negative, and those at the negative side must be positive. The term "ELECTRO" is often used in this connection; thus, zinc is *electro-positive;* chlorine is *electro-negative.*

As the list of known elements is limited, there will be two bodies which, by their high affinities, will stand at the extremes of the scale, one being negative, the other positive. Leaving out of consideration some rare elements, potassium is the most positive, oxygen the most negative.

The relations of electricity to chemistry have been studied by the action of electric currents passing through liquids containing known compounds. Generally the experiments are carried out on solutions in water, but similar results may often be obtained by passing the current through melted substances. The latter method will not be specially considered here. In testing the action of electricity the solution is usually contained in a vessel called the "decomposing cell." The terminals (*poles*), through which the current enters and leaves the liquid, are usually made of carbon or platinum, to resist corrosion. Many experiments have been made and it has been found that substances are of two classes, those that conduct the current and are decomposed by it (*electrolytes*) and those that do not conduct it and are not decomposed by it (*non-electrolytes*).

Among the former class (electrolytes) are all the substances termed acids, bases and salts; among the latter class are many organic bodies, such as albumin, sugar and starch.

Osmotic Pressure. Ions.—When two solutions of the same substance, but of different concentrations (that is, containing different proportions in the same volume of liquid), are brought in contact, a flow takes place, by which in time the two will lie entirely mingled. The energy with which one solution pushes its way into the other is called "osmotic pressure" (osmotic, from a Greek word, meaning "to thrust"). With any given substance, the pressure has a definite relation to the amount of the substance in a certain volume of the solution, which is expressed by saying that "osmotic pressure is proportional to the concentration." The phenomenon is often shown by filling a bladder with a mixture of alcohol and water, tying tightly and immersing in water. The bladder gradually swells and will ultimately burst. Many other substances may be used and similar results obtained. The swelling is due to the fact that the water can pass through the pores of the animal membrane but the alcohol cannot. For this reason the membrane is termed, "semi-permeable," that is, it allows some substances to pass but others not.

The cause and character of osmotic pressure have been extensively studied of late, the semi-permeable membrane used being generally copper ferrocyanide precipitated in the pores of vessels made of unglazed por-

celain or earthenware. This method is used because the pressure is often very high and ordinary animal or vegetable membranes will not withstand it.

Among the results of investigations is the fact that solutions of electrolytes have a higher osmotic pressure in proportion to concentration than solutions of non-electrolytes. Moreover, this difference is more marked as the solutions are more dilute. Reasoning from such facts, chemists have inclined to the view that in solutions of electrolytes a modification of the molecules has occurred by which two groups are developed from each molecule, one group charged with positive electricity and the other with negative. With non-electrolytes no such modification occurs and the osmotic pressure is due entirely to the molecule in its original condition. For example, it is now generally held that a solution of sodium chloride contains sodium atoms positively charged and chlorine atoms negatively charged, but a solution of sugar has no such condition. The modification is due to the dissolving liquid, and is, therefore, greater in proportion to the liquid present; that is, the more dilute the solution, the greater the number of molecules changed.

It must especially be borne in mind that this development of electrical charges takes place by the mere act of solution and does not require the introduction of any electrical current.

The groups are termed "*ions*" and the condition "*ionization*" or "*electrolytic dissociation.*" The chemical activity of many compounds is dependent on their degree of ionization. Among other instances, the general chemical activity of an acid is so conditioned; an acid which ionizes in large proportion is active, an acid that ionizes but slightly is feeble.

Water is the most powerful ionizing liquid known. Common alcohol is much feebler; hence, solutions made with alcohol often differ markedly in chemical action from those made in water.

As ionization of any given substance produces only two groups, respectively positive and negative, it is obvious that in compounds containing more than two elements, at least one of the ions must be composite. In many cases the point of division will depend on the dilution. The formulas given below illustrate this. Ionization is shown by separating the groups by a comma and marking each with the proper sign.

Sodium chloride $\overset{+}{\text{Na}}, \overset{-}{\text{Cl}}$

Hydrochloric acid $\overset{+}{\text{H}}, \overset{-}{\text{Cl}}$

Potassium chloroplatinate $\overset{+}{\text{K}_2}, \overset{-}{\text{PtCl}_6}$

Sulphuric acid (slightly diluted) $\overset{+}{\text{H}}, \overset{-}{\text{HSO}_4}$

Sulphuric acid (much diluted) $\overset{+}{\text{H}_2}, \overset{-}{\text{SO}_4}$

Important applications of these principles are given in connection with the study of acids and bases.

It is upon the existence of ions that the power of an electric current to decompose substances depends. When, for instance, a current of electricity is passed into a solution of sodium chloride the positive ions "migrate" to the negative pole, the negative ions to the positive, under the usual law of attraction between unlike affinities. When the current is introduced into a solution of gelatin, no decomposition occurs, for no ions exist. Water ionizes itself, but only in very minute amounts, so that pure water is ordinarily not considered an electrolyte. These statements, however, do not apply to cases in which currents of electricity act by producing great heat.

REACTIONS

Chemical symbols are employed not only to show composition, but also to show exactly the nature of the chemical changes which occur when different substances are brought in contact. When so used, the expression is called a REACTION. Strictly speaking, the statement in symbols is the "equation of the reaction," but the shorter term is generally used. Some compounds, much used for producing reactions, are called REAGENTS. When vinegar is poured upon marble, it is usually said that the marble is corroded, but, in fact, the vinegar is equally acted upon. Both substances are changed in composition, both are rendered unfit for their original uses; in other words they have not only acted, they have reacted, and are, therefore, both reagents.

A reaction is substantially an expression of the results of an experiment, and, when correctly written, gives the proportion in which bodies are to be used and the proportion of the resulting substances. Speaking absolutely, the correctness of any equation is not assured until the experiment is made and the result analyzed; but the progress of chemistry has made known certain laws of change, which enable one to predict, or infer, many results without the necessity of actual observation. Every now and then, however, the analogy fails, and experiment disappoints the suggestions of theory.

Reactions are written by placing in proper proportion and connected by + signs the formulas of the bodies concerned, then writing the sign = or → and following this by the formulas of the resulting bodies. For instance,

$$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$$

expresses that on bringing together silver nitrate and hydrochloric acid, a chemical change occurs by which silver chloride and nitric acid are produced. This statement also shows the exact relations by weight in which the substances react, so that if, for example, the amount of silver nitrate used is known, the amount of sodium nitrate and silver chloride produced can be calculated. (See later, under "Stoichiometry.)

The sign = is often used with reactions, but to avoid suggestion of algebraic equations the sign → is coming into use. It will be used in this work; it should be read "produces" or "results in." In writing reactions, three difficulties are encountered: 1st. To know whether a given change will take place. 2d. To know the quantities of the bodies to be used. 3d. To know the nature of the resulting bodies. These difficulties may be taken up in order. 1st. In the simplest cases, the nature of the reaction will be determined by the affinities of the elements as governed by their electrical relations, the change taking place in such a way that the element having the stronger electric affinity will drive out and supplant the element of similar but weaker affinity. When chlorine acts upon the bromides they are decomposed, the bromine being expelled, and bromine in turn, expels iodine from combination. Therefore, such reactions as

$$KBr + Cl \rightarrow KCl + Br$$
$$KI + Br \rightarrow KBr + I$$

are simply illustrations of the general electrical relations of elements concerned. If these affinities were the only active causes of chemical change, the subject would be quite simple, but circumstances may modify the play of affinities, so as to produce an endless variety of chemical action. All the modifying influences are not yet known, but some of them are understood, and are of importance.

(*a*) **Insolubility.**—When in any liquid substances are brought together which are capable of forming a body insoluble in the liquid, that insoluble compound will be produced in spite of the general relations of affinities. This influence of insolubility is the basis of a large number of tests and other chemical operations.

When the formation of the insoluble compound would require a powerful chemical agent to be set free, the change will not take place, unless, of course, the added substance is stronger than the one to be liberated. Carbonic acid forms with calcium a body nearly insoluble in water, but this body cannot be formed by passing carbonic acid into calcium sulphate.

The reason is shown at once by examining the conditions of the experiment. The reaction would have to be $CaSO_4 + H_2CO_3 \rightarrow CaCO_3$ (insoluble) + H_2SO_4, that is, sulphuric acid would be set free. The activity of H_2CO_3 is, under ordinary conditions, so much below that of H_2SO_4 (see pp. 24, 25, 26) that the former will not drive out the latter. The condition becomes changed if the action of the carbonic acid is assisted by some substance which will react with sulphuric acid and will prevent it being set free. $CaSO_4 + Na_2CO_3$ will produce immediate action, resulting in $CaCO_3 + Na_2SO_4$. This reaction illustrates a common method of keeping the powerful affinities in abeyance, and thus allowing secondary influences full play. Some of the arsenic tests show the principle strikingly. Arsenous acid added to copper sulphate produces no action, because the affinity of the SO_4 is too strong, but by adding a little alkali, the strong affinity this has for SO_4 assists in breaking up the copper sulphate and immediately a precipitate of copper arsenite falls.

(*b*) **Volatility.**—This is the second influence that disturbs ordinary affinities. If a body is capable of being converted into a gas, this fact will diminish its chemical power; fixed substances that have ordinarily less affinity will drive it out of combination. Boric acid, for instance, is one of the weak acids, yet at a red heat it will decompose sulphates. The cause is, in the main, that at this temperature sulphuric acid is volatile, while boric acid is fixed.

The ease with which hydrogen is driven out of combination may be regarded as due to its volatility, as it is a gas even at low temperatures.

(*c*) **Concentration.**—Chemical action is often governed by the proportion of substances. If water vapor is passed over red-hot iron, iron oxide is formed and hydrogen is set free; if the hydrogen is passed back over the iron oxide, steam is formed and iron set free. In the first case, the water is in excess, and exerts an oxidizing influence; in the second, the hydrogen is in excess, and exerts a deoxidizing influence.

It will be seen to be a deduction from these statements that no substance can be set down as absolutely the strongest in affinity. Chemists cannot determine, for instance, what is the strongest acid or the strongest alkali, except under specified conditions. Under ordinary conditions, the greater the degree of ionization, the stronger the acid or base. Sulphuric acid ionizes readily, hence is a very strong acid.

2d. The proportion in which bodies react is determined by their valencies. Let it be required to write the reaction between mercuric chloride and potassium iodide. The formulas are $HgCl_2$ and KI, but the bodies

will not react in this proportion, for the Hg will require I_2 and Cl_2 will require K_2. The proper reaction is $HgCl_2 + 2KI = HgI_2 + 2KCl$. In the same way, antimonous sulphide and hydrochloric acid can only act upon each other in the ratio $Sb_2S_3 + 6HCl$ because Sb being a triad, Sb_2 will combine with Cl_6, and S being a dyad, S_3 will require H_6.

3d. If a chemical change occurs when two given substances are brought in contact, the nature of it will depend principally upon the electrical relations of the ions concerned. In the reaction $HgCl_2 + H_2S$, the only possible result is the combination of S with Hg and H with Cl, as is shown at once by placing the proper signs over the elements, thus, $\overset{+\ -}{HgCl_2}\ \ \overset{+\ -}{H_2S}$.

$$\overset{+\ +}{\quad}\ \ \overset{-\ -}{\quad}$$

Such a combination as HgH_2 or Cl_2S is improbable, since like electricities do not attract. In beginning with reactions, the student will do well to place the proper signs over the ions, and these will be a useful guide and control. When acids or salts, containing three elements, are part of the reaction, the positive sign is put over the hydrogen or the metal, and the negative sign over the remaining elements—

$$\overset{+\ -}{Ba(NO_3)_2} + \overset{+\ -}{K_2SO_4} \rightarrow \overset{+\ -}{BaSO_4} + \overset{+\ -}{2KNO_3}$$

The placing of the single sign over two elements is simply an evidence of the fact that in ordinary reactions these two elements act as a unit, that is, an ion.

The following formulas will further illustrate the general principle:—

$$\overset{+\ -}{AgNO_3} + \overset{+\ -}{NaCl} \rightarrow \overset{+\ -}{AgCl} + \overset{+\ -}{NaNO_3}$$

$$\overset{+\ -}{H_2O} + \overset{\ \ -}{Cl_2} \rightarrow \overset{+\ -}{2HCl} + \overset{\ \ -}{O}$$

$$\overset{+\ -}{BaCl_2} + \overset{+\ +\ -}{KHSO_4} \rightarrow \overset{+\ -}{BaSO_4} + \overset{+\ -}{KCl} + \overset{+\ -}{HCl}$$

In the last reaction, the electro-positives K and H may seem to be in union, but this is not the case. Each is independently united to the SO_4, which is a dyad. The formula might be written—

$$\begin{matrix} K \\ H \end{matrix} SO_4.$$

Reversible Reactions.—Many reactions can take place in either direction, that is, the products under given conditions will under other conditions produce the original substances. The experiments mentioned

in the paragraph on "concentration" on p. 19 are instances. When steam is passed over hot iron the effect is represented thus:

$$Fe_3 + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$

When hydrogen is passed over the iron oxide the reaction is

$$Fe_3O_4 + 4H_2 \rightarrow Fe_3 + 4H_2O$$

Both actions can, therefore, be expressed in one statement, thus:

$$Fe_3 + 4H_2O \leftrightarrows Fe_3O_4 + 4H_2$$

Usually one of the reactions is more likely to occur than the other and this may be indicated, if desired, by a heavier arrow.

Catalysis.—This phase of chemical action has attracted a great deal of attention of late years, many important industrial processes being dependent on it. It is the bringing about of chemical action by a substance that is left at the close of the action in practically the same form and amount as at the beginning. A substance that acts in this manner is called a *catalyst*. The word was coined by Berzelius in 1836. Catalysts may be either inorganic or organic. Organic catalysts are usually called *enzyms* and a description of the most important will be found under that title in the organic section. In 1832, Döbereiner discovered that a small amount of manganese dioxide has the power to cause the decomposition of potassium chlorate at a much lower temperature than with the pure material (see under oxygen). Spongy platinum and platinum black, finely divided forms of the metal have the power to bring about combination of oxygen with hydrogen and sulphur dioxide (see under sulphuric acid). The method by which catalysts act is not known. Organic catalysts in the great majority of cases cause the association of water molecules with the molecules of the other substance, which association then breaks up into new substances. Thus the enzym (catalyst) of yeast causes common sugar to take up water and break into two new molecules, dextrose and levulose (see under sucrose).

RADICALS

A radical is any group of atoms having unsatisfied valency; the number of the unsatisfied degrees is the valency of the radical. The following formulas illustrate the principle. The degrees outside the parentheses indicate in each case the valency of the radical, being the difference between the valencies of the constituent atoms:—

$$\left(\overset{\text{V II}}{NO_3}\right)^{I} \quad \left(\overset{\text{V II}}{NO_2}\right)^{I} \quad \left(\overset{\text{IV III}}{CN}\right)^{I} \quad \left(\overset{\text{IV II}}{CO}\right)^{II} \quad \left(\overset{\text{I II}}{HO}\right)^{I} \quad \left(\overset{\text{I IV}}{HC}\right)^{III}$$

The electrical relations of a radical are generally determined by the electrical character of the preponderating valency, but not invariably. While the combining capacity and general functions are dependent on the unsaturated valency, yet, in chemical combinations, the whole molecule takes part, and hence the electrical character is influenced by that of each atom present. Thus in $\left(\overset{V\ I}{NH_4}\right)^{I}$ it may seem that the nitrogen valency would only give to the radical indifferent or intermediate electrical relations, but experiment shows that this is a group having distinctly positive affinities; the four atoms of positive hydrogen, though insufficient to saturate all of the nitrogen valency, yet impress on the molecule their function.

In many cases the influence of the preponderating valency is more decided. Thus in $\left(\overset{V\ II}{NO_3}\right)$ the oxygen valency is in excess, and the radical is negative.

The general chemical relations of radicals depend on ionization. If the compounds containing them ionize readily and to a large extent, the solutions will be active and each radical will take part in reactions as an element. If the compound does not ionize the radicals will not react readily.

The compounds of carbon show very well the principle on which the valency of a radical depends:—

$\overset{IV}{H_4C}$	Saturated.
H_3C	Monad.
H_2C	Dyad.
HC	Triad.
C	Tetrad.

The last is the free element which might be regarded as the final radical, so that there are elemental radicals and compound radicals, but the term is usually limited to the latter signification.

The following formulas give the compositions, valencies and names of some important radicals:—

NH_4	Ammonium	Monad.
NH_2	Amidogen	"
HO	Hydroxyl	"
HS	Hydrosulphyl	"
CN	Cyanogen	"
H_3C	Methyl	"
CO	Carbonyl	Dyad.
$COOH$	Carboxyl	Monad.

ACIDS, BASES AND SALTS

Acids are compounds that ionize so as to give one or more ions containing hydrogen only. In all of them, in the non-ionized state, the hydrogen is united directly to negative elements. Two important classes of acids may be distinguished.

Hydrogen acids—commonly called hydro-acids—

HCl ..... Hydrochloric acid.
HBr ..... Hydrobromic acid.
HI ..... Hydriodic acid.
HF ..... Hydrofluoric acid.

Oxygen acids—

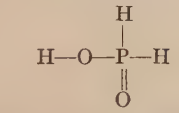
H_2SO_4 ..... Sulphuric acid.
HNO_3 ..... Nitric acid.
H_3PO_4 ..... Phosphoric acid.
H_2CO_3 ..... Carbonic acid.
$HClO_3$ ..... Chloric acid.

Experiment shows that in each of the oxygen acids, the hydrogen is in more direct relation with some oxygen atoms than with the rest of the molecule, so that they may be formulated as follows:—

$$(HO)_2SO_2 \quad (HO)NO_2 \quad (HO)_3PO \quad (HO)_2CO \quad (HO)ClO_2$$

It will be seen that in the non-ionized state all the hydrogen is in the form of hydroxyl.

Hydrogen which is not in this condition in a molecule is not easily replaceable by a positive element. Thus in HCl the hydrogen is easily replaceable by a positive, but not in NH_3. The two conditions of hydrogen may co-exist in a molecule. In hypophosphorous acid, H_3PO_2, experiment shows that only one hydrogen atom is easily replaceable, and the arrangement is considered to be as follows:—



Only one hydrogen atom is directly united to a strongly negative element.

It must not be overlooked that the above formulas represent merely the non-ionized acids, and, therefore, show them in the inactive con-

dition. On complete ionization, hydrogen becomes the positive ion, and the oxygen forms, with the other elements, the negative ion. Hydrogen, that is not associated in the original molecule with a negative substance or group, also remains in the negative ion. The number of hydrogen ions that are produced from any given acid determines the basicity of the acid. The above formulas are re-arranged thus on ionization:

Name	Empirical formula	Rational formula	Ionization formula + −	Basicity
Sulphuric acid	H_2SO_4	$(HO)_2SO_2$	H_2,SO_4	dibasic
Nitric acid	HNO_3	$(HO)NO_2$	$H\ ,NO_3$	monobasic
Phosphoric acid	H_3PO_4	$(HO)_3PO$	H_3,PO_4	tribasic
Carbonic acid	H_2CO_3	$(HO)_2CO$	H_2,CO_3	dibasic
Chloric acid	$HClO_3$	$(HO)ClO_3$	$H\ ,ClO_3$	monobasic
Hypophosphorous acid	H_3PO_2	$(HO)PH_2O$	$H\ ,PH_2O_2$	monobasic

Differences in the position and function of hydrogen in the same molecule are unusual in the inorganic acids, which generally have all their hydrogen in either the hydroxyl position or in some similar relation, but nearly all organic acids contain hydrogen which is not replaceable.

In thiocarbonic acid, H_2CS_3, in which sulphur takes the place of oxygen, the non-ionized arrangement is $(HS)_2CS$. Sulphur, selenium and tellurium may in the same manner take the place of oxygen in the molecule and render the hydrogen replaceable.

When the molecule contains bodies of high positive character, the power of replacing the hydrogen by other positives does not exist, unless several molecules of oxygen (or S, Se or Te) are also present. It appears then that as the proportion of oxygen is increased in any molecule, without other change, its acid character will be gradually developed. Thus, $Cr(OH)_2$ possesses no acid character, but if two atoms of oxygen are added to the chromium, making $(HO)_2CrO_2$, that is, H_2CrO_4, a well marked acid, chromic acid, is produced. It is then according to the number and position of the negative elements in any molecule that the function of the hydrogen is determined. When strongly positive elements are present, either without negatives or with only relatively few atoms of them, the hydrogen is not easily replaceable by positives, the body is not an acid, but has power to interact with acids and neutralize them. Thus the above mentioned compound, $Cr(HO)_2$, will dissolve easily in sulphuric acid and neutralize it, that is, take away the characteristic proper-

ties of the acid, the sour taste, effect on organic colors (see below), and general chemical activity. Substances that act in this manner are called *bases*. The action in the case of chromous hydroxide and sulphuric acid would be thus represented:—

$$Cr(HO)_2 + H_2SO_4 \rightarrow CrSO_4 + 2H_2O.$$

The activity of these bases depends like the activity of acids upon the ionization. The hydrogen in the present case, however, does not become the positive ion, but remains with the oxygen (or other member of the oxygen group). The following examples will illustrate these points:—

Name	Empirical formula	Rational formula	Ionization formula + −	Acidicity
Sodium hydroxide	$NaHO$	$NaOH$	Na,OH	monacid
Barium hydroxide	BaH_2O_2	$Ba(OH)_2$	$Ba,(OH)_2$	diacid

When acids and bases are mixed, mutual re-arrangements occur. The hydrogen ions of the acid combine with the hydroxyl ions of the base; the positive ions of the base combine with the negative ions of the acid. The resulting compounds as will be seen by the annexed reactions are water and a compound derived from the acid by substitution of its hydrogen by some other positive. These latter compounds are called "*salts*." If the amount of base is not sufficient for complete reaction, only part of the hydrogen ion of the acid is removed, and an *acid salt* is produced. If the amount of base is larger than required, some of it is left unchanged. The reacting substances are largely ionized, but one of the products, water, is but slightly ionized (see p. 16); it follows that a discharge of energy must occur in such reactions. This is usually manifested in the form of heat, reactions of the type shown below being always attended by evolution of heat. Such a reaction is termed *exothermic*. Reactions attended by absorption of heat (which are unusual) are termed *endothermic*. Care must be taken not to confuse the term "salt" with the common name of sodium chloride

Illustrative reactions:

Base	Acid	Salt	Water
$NaHO$	$+ HCl$	$\rightarrow NaCl$	$+ H_2O.$
$NaHO$	$+ H_2SO_4$	$\rightarrow NaHSO_4$	$+ H_2O.$
$2NaHO$	$+ H_2SO_4$	$\rightarrow Na_2SO_4$	$+ 2H_2O.$
KHO	$+ HNO_3$	$\rightarrow KNO_3$	$+ H_2O.$
$Cu(HO)_2$	$+ H_2SO_4$	$\rightarrow CuSO_4$	$+ 2H_2O.$
$Bi(HO)_3$	$+ 3HCl$	$\rightarrow BiCl_3$	$+ 3H_2O.$
$Fe_2(HO)_6$	$+ 3H_2SO_4$	$\rightarrow Fe_2(SO_4)_3$	$+ 6H_2O.$

A salt may, therefore, be defined as the result of the interaction of an acid with a base.

Since the function of the base in these reactions depends essentially on the strongly positive element, it is not necessary to have it in association with hydroxyl. The formation of salts may take place by the action of acids upon oxides, upon the elements themselves, and also upon compounds containing weaker acid radicals than those existing in the acid employed. Zinc sulphate, for instance, may be made by any of the following methods:—

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2.$$
$$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O.$$
$$Zn(HO)_2 + H_2SO_4 \rightarrow ZnSO_4 + 2H_2O.$$
$$ZnCO_3 + H_2SO_4 \rightarrow ZnSO_4 + H_2O + CO_2.$$

Theoretically, therefore, and frequently practically, there may be many methods of producing salt, but in many cases the affinity of the acid radical is not sufficient to bring about the change, unless the positive is either in the form of oxide or hydroxide. Thus the reaction—

$$Ag + HCl \rightarrow AgCl + H$$

will not occur, but either

$$AgHO + HCl \rightarrow AgCl + H_2O,$$
$$\text{or } Ag_2O + 2HCl \rightarrow 2AgCl + H_2O$$

will occur.

Intimately connected with this subject is the meaning of the term *acid*, *alkaline* and *neutral*, as applied to the conditions of substances. If a drop of sulphuric acid is added to a solution of litmus, the liquid turns red; by the addition of sodium hydroxide the color will be restored. The sodium hydroxide is a base; it has interacted with the acid and deprived it of its chemical activity. By this combination the sodium hydroxide is also neutralized.

Litmus is a color much used for these tests. It becomes red on the addition of an acid, and has the blue color restored on the addition of a base. It is usually sold in the blue condition, and is used either in solution in water or in the form of *litmus paper*—strips of paper soaked in the solution and dried.

A number of artificial colors from coal-tar products are now used as substitutes for litmus. Among these are:—

Phenolphthalein—red when alkaline, nearly colorless when acid.

Congo red—red when alkaline, blue when acid.

Lakmoid—similar changes to litmus.

Methyl orange—pale yellow with acids, pink with alkalies.

These color reactions are of importance in practical chemical operations, but they have little value in determining the theoretical relations between acids, bases and salts, since there are substances which are theoretically acids, yet act on the colors as if alkaline, and the reverse.

The ion of an acid is sometimes called the residue of the acid. For instance SO_4 is the residue of sulphuric acid; NO_3 is the residue of nitric acid. The acid radical proper is the body obtained by deducting all the hydroxyl or hydrosulphyl, etc., from the acid. SO_2 is the radical proper of sulphuric acid. This distinction in nomenclature is convenient in expressing some of the reactions of these acids. Some writers now use the word "ion" as a termination indicating a negative ion, thus, SO_4 is called "sulphion," NO_3, "nitrion."

Acidity and Alkalinity in Special Relations.—In connection with the great development of physiologic chemistry of recent years, both in animals and plants, several important relationships have been established which require careful attention by the student.

STANDARD SOLUTIONS.—Solutions of known strength are termed "standard." The most important types are those based on the molecular weight of the substance. It is especially with acids and alkalies that the method is applied. The starting point in strength is the "normal" solution.

A normal solution is one that contains in 1000 c.c. as many grams of the substance as are equal to its molecular weight divided by the number of *active* hydrogen atoms which it contains or to which it is equivalent. By *active* hydrogen is meant hydrogen that is ionizable. The following examples will make the definition clear.

Hydrochloric acid is HCl. It contains, but 1 active hydrogen atom. A normal hydrochloric acid will, therefore, consist of 36.46 grams of the acid in 1000 c.c. of solution. (Note especially that this is not made by adding 36.46 grams to 1000 c.c. but by diluting the commercial solution of the acid with water in amount sufficient to make a solution of the stated strength.)

Sulphuric acid is H_2SO_4. Its molecular weight is 98, but as it contains 2 atoms of ionizable hydrogen, this weight must be divided by 2, so that a normal sulphuric acid contains 49 grams of acid in 1000 c.c.

Phosphoric acid is H_3PO_4. Its molecular weight is 98, but it contains 3 atoms of ionizable hydrogen so its normal solution contains 32.66 grams of acid in 1000 c.c.

Acetic acid is $C_2H_4O_2$. Its molecular weight is 60. Of its 4 hydrogen atoms only 1 is ionizable; the other three are directly united to the carbon, (see p. 138) so that a normal acetic acid will contain 60 grams of acid in 1000 c.c.

These principles are applied also to alkalies.

Sodium hydroxide is NaOH. Its molecular weight is 40. It has, strictly speaking, no ionizable hydrogen, but one molecule of the alkali is equivalent to 1 molecule of hydrochloric acid, hence normal sodium hydroxide will contain 40 grams of hydroxide in 1000 c.c. of liquid.

Barium hydroxide is BaH_2O_2. Its molecular weight is 171, 1 molecule of barium is equivalent to 2 molecules of hydrochloric acid, hence normal barium hydroxide will contain 85.5 grams of the substance in 1000 c.c. It will be seen by this series of examples that normal solutions are equivalent to each other and this is the great advantage in their use.

If we take such a salt as potassium permanganate, it seems to be out the line as it contains no hydrogen, but its principal function is an oxidizing agent towards hydrogen or some equivalent positive. Therefore, the phrase (of the definition of normal solution) "to which it is equivalent," will be applicable. The oxidizing power of permanganate is dependent of the following reaction:

$$2KMnO_4 \rightarrow K_2O + 2MnO - O_5$$

which, however, does not occur unless some acid is present to combine with the potassium and manganous oxides. The actual change is shown in the reaction with oxalic acid.

Potassium permanganate	Sulphuric acid	Oxalic acid	Potassium sulphate	Manganous sulphate		

$$2KMnO_4 + 3H_2SO_4 + {}_5H_2C_2O_4 \rightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

It will be noted that 1 molecule of permanganate gives up oxygen sufficient to oxidize 10 atoms of hydrogen or equivalent, hence a normal solution will be 31.6 grams of potassium permanganate in 1000 c.c. when the solution is intended for oxidizing purposes, 316 being the weight of 2 molecules.

Standard solutions of the types above noted are of extensive use in volumetric analysis, an important department of practical chemistry. For most purposes the normal solution is too strong, and dilutions of it to different degrees are used. Of these the one-tenth strength—decinormal—is common, but one-hundredth—centinormal—is occasionally used. Intermediate degrees such as one-third normal are sometimes used.

The symbol N is employed N/1 is a normal solution; N/10, decinormal; N/3, one-third normal; 2N, twice normal and so on.

The equivalent relations between standard solutions apply only to reactions of definite nature such as neutralization, oxidation and reduction. When the reactions of acids, alkalies or salts towards living tissues are in consideration an entirely different condition prevails. In these cases the degree of ionization becomes of great moment.

HYDROGEN-ION CONCENTRATION

This term, which has become of very frequent use in bio-chemistry, represents conditions which are of great importance is the study of acids and alkalies in their effects on living tissues. Solutions of all ionizable substances differ much as to the degree of ionization under the same conditions of temperature and dilution. Acids and alkalies show such differences very markedly. For instance, in N/1 nitric acid the ionization amounts to over three quarters of the acid molecules while in N/1 acetic acid only about one molecule in three hundred is ionized. Notwithstanding this difference, if we titrate both acids against N/1 sodium hydroxide, the same amount of each will be required. This is because as fast as the ionized acetic acid is neutralized other molecules assume electric charges and are ready for the action of the alkali, this action going on until all the acid is neutralized.

The conditions are, however, very different when the acids or alkalis are in contact with living tissue which cannot neutralize them. The action on the tissue is materially dependent on the degree of ionization, so that the determination of this degree becomes important. Common vinegar is a 4% solution of acetic acid, and is quite agreeable to the taste. A 4% solution of nitric acid is quite disagreeable. The difference lies almost entirely in the degree of ionization of the two acids, the molecular weight of them being nearly the same (nitric, 63; acetic, 60).

In these studies water is always taken as the ionizing agent as it is the fluid which is contained in living organisms. Other liquids have ionizing actions but are not important. The degree of ionization is measured by the electric conductivity, for the current is passed through liquids by the ions, and the more there are of these in a given volume the more easily is the current carried, "Many hands make light work."

It is necessary to have standards of comparison and a system of symbols. The system in use is somewhat complicated but its general acceptance is ensured. As a point of departure a solution containing 1 gram of

ionized hydrogen in 1 liter is taken as unity. To express this the *logarithm* of unity not unity itself is used. The symbol generally adopted by American chemists is pH. The logarithm of unity is zero, so the solution containing 1 gram of ionized hydrogen is represented by pH_0. Weaker solutions than this are represented by the logarithms of fractions which are minus figures. A solution of 0.1 gram of *ionized* hydrogen in 1 liter would be represented by pH − 1. In practice for the sake of simplicity the minus sign is omitted, so that the somewhat awkward form is developed that as the dilution increases the exponent seems to increase.

The following table will show the relations:

Grams of ionized hydrogen in 1 liter	Notation	Reaction
1.0	pH_0	acid
0.1	pH_1	"
0.01	pH_2	"
0.001	pH_3	"
0.0001	pH_4	"
0.00001	pH_5	"
0.000001	pH_6	"
0.0000001	pH_7	

The last figure has been found to be that of pure water, by its self-ionization, and pH_7 is therefore neutrality. No further decrease of hydrogen-ion concentration can be obtained except by addition of hydroxyl ions. The condition at pH_7 is $\overset{+}{H}, \overset{-}{HO}$, the liquid contains in ten million liters 1 gram of *ionized* hydrogen and 17 grams of *ionized* hydroxyl, that is 18 grams of water in ten million liters are self-ionized. If, therefore, substances yielding hydroxyl ions and not hydrogen ions are added, the dilution of the latter will proceed so that we will have the following series of *alkaline* solutions

Grams of ionized hydrogen in liter of liquid	Notation	Reaction
10^{-8}	pH_8	Alkaline
10^{-9}	pH_9	"
10^{-10}	pH_{10}	"
10^{-11}	pH_{11}	"
10^{-12}	pH_{12}	"
10^{-13}	pH_{13}	"
10^{-14}	pH_{14}	"

In the first column minus exponents are used to avoid many ciphers.

The last solution contains 17 grams of *ionized* hydroxyl, such would be obtained if 40 grams of sodium hydroxide (Na = 23, HO = 17) were present in the liter of solution and *completely* ionized.

The notation affords a method for indicating the degree acidity or alkalinity so far as *ionization* is concerned. Thus, pH_6 is acidity; pH_9 is alkalinity, but such symbols *do not express the actual amount of free acid or alkali in a solution.* For such data, the titration must be made with indicators; acids being titrated with standard alkali and alkalies with standard acids.

No acid in common use ionizes to such extent that its *normal* solution contains 1 gram of *ionized* hydrogen. Hydrochloric acid is most active in this respect about 90% of the molecules assuming the electrical charges. Nitric acid is somewhat less ionized; acetic, boric, and silicic are among the least active, only small proportions of their molecules being changed. Temperature affects the degree of ionization, also dilution. Ordinary data are assumed to be at 20° C. The degree to which an acid or an alkali iconizes determines largely the question whether it is "strong or weak" in common phrase. Nitric, hydrochloric and sulphuric acid are strong (highly ionized) acetic, boric and silicic are feeble (slightly ionized). Similarly, sodium and potassium hydroxides ionize largely are strong caustics; ammonium hydroxide much less and is, therefore, a much weaker caustic.

These relations, however are much modified by incidental conditions. Boric acid, for instance, is capable of expelling sulphuric acid at a high temperature when the latter is volatile. These questions are discussed on page 19. Specific physiologic actions also interfere. Barium hydroxide is much less ionized than sodium hydroxide in similar solutions but soluble barium salts have a specific poisonous property so that very weak barium hydroxide may do more harm when swallowed than very weak sodium hydroxide.

Applications of the principle of ion-concentration will be found in the section on Clinical Chemistry.

The critical method of determining ionization is by electric conductivity, but research has brought into use a number of colors of the coal-tar-color type, that respond to certain ion-concentrations and these are now largely used for approximate determinations.

For brevity, the term "hydrion-concentration" has been suggested.

Salts may be divided into four classes:—

NORMAL SALTS, in which the hydrogen of the acid is replaced by a single element, according to its valencies. The acids themselves are normal salts of hydrogen:—

Na_2CS_3..... Sodium thiocarbonate.
KNO_3..... Potassium nitrate.

MIXED SALTS, in which two or more positives are present. When some replaceable hydrogen remains, the body is usually called an *acid* salt:—

$HKCO_3$..... Acid potassium carbonate.
$KNaSO_4$..... Sodium potassium sulphate.

DOUBLE SALTS, in which two complete salts of either of the above classes unite to form a definite compound, which is generally distinctly crystalline:

$FeSO_4,(NH_4)_2SO_4$..... Ammonium ferrous sulphate.

OXY SALTS (sometimes called *basic* salts or *sub* salts), in which oxygen takes the place of one or more of the acid radicals:—

$BiONO_3$..... Bismuth oxynitrate.
SbOCl..... Antimony oxychlorid.

VOLUME COMBINATION

If equal volumes of elements in the gaseous state are weighed under the same conditions, the relative weights will, with a few exceptions, be in exact proportion to their atomic weights. For instance, a vessel which holds 1.008 grain of hydrogen (about 47 cubic inches) will hold the following quantities of other elements, it being understood that all the bodies are in the state of gas and at the same temperature and pressure:—

Element	Atomic weight	Wt. of vol. equal to vol. of H
O	16	16
S	32	32
Cl	35.46	35.46
I	126.9	126.9
Br	80	80

Some of the elements cannot be converted into vapor, and consequently cannot be compared on this system. Among these are carbon, silicon and many of the common metals. These practically resist the action of the highest temperature which can be used in such experiments.

A few elements show results which are exceptional; among these are—

Element	Atomic weight	Wt. of vol. equal to vol. of H
As	75	150
P	31	62
Hg	200	100

In the case of phosphorus and arsenic the weight is twice as great as analogy would require; in the case of mercury, half as great.

The following general law has been established by mathematical and physical investigation: *Equal volumes of elementary gases contain equal numbers of molecules.*

The relative weight of the atoms of each element may be determined by this law. If a given volume of hydrogen contains, say, 1000 molecules, the same volume of oxygen will contain the same number; and as the oxygen volume is 15.88 times as high as the hydrogen, it is clear that the weight of each molecule of oxygen will be 15.88 times that of each molecule of hydrogen. The molecules of hydrogen and oxygen each contain two atoms, hence, the atomic weights will also be in the proportion of 15.88 to 1 (16 to 1.008; see p. 3).

In gases the spaces between the molecules are very large in proportion to the size of the great molecules themselves. Elementary gases combine so as to produce a volume of gas *which is equal to twice the volume that would be occupied by one atomic weight of hydrogen.* The following instances are taken from among the commonest chemical compounds:—

One volume of H and one volume of Cl combine and produce *two* volumes of HCl.

Two volumes of H and one volume of O combine and produce *two* volumes of H_2O.

Three volumes of H and one volume of N combine and produce *two* volumes of NH_3.

Some examples will make this plain:—

47 cubic inches of H, weighing 1 grain, will combine with 47 cubic inches of Cl, weighing 35.5 grains, and produce 94 cubic inches (*i. e.*, 47×2) of hydrochloric acid (HCl), weighing 36.5 grains. The ratio of weights of equal bulks of hydrochloric acid and hydrogen is not 94 to 1, for the figure 94 is calculated for a molecule of HCl, while 1 represents an atom of H. Molecule must be compared to molecule, that is HCl to HH, hence 94 to 2 : : 47 to 1. By dividing 36.5 by 2 the weight of a quantity of hydrochloric acid equal to one atomic weight of hydrogen—viz., 18.25,

is obtained. This figure represents, therefore, the density or specific gravity compared to hydrogen.

94 cubic inches of H, weighing 2 grains, will combine with 47 cubic inches of O, weighing 15.88 grains, and produce 94 cubic inches of steam, H_2O, weighing 17.88 grains. Dividing 17.88 by 2, gives, as before, the density of steam compared to hydrogen—viz., 8.94.

47 cubic inches of N, weighing 14 grains, will combine with 141 cubic inches (47×3) of H, weighing 3 grains, and form 94 cubic inches of ammonia, NH_3, weighing 17 grains; and this weight, divided by 2, gives 8.5 as the density of ammonia compared to hydrogen.

These principles are employed in determining formulas N and O combine to form a body called nitric oxide which is sometimes written NO and sometimes N_2O_2. The following calculation will show which is correct:—

The formula NO requires—

One volume of N	= 14	
" " " O	= 16	
	30	$30 \div 2 = 15$

The formula N_2O_2 will require—

Two volumes of N	= 28	
" " " O	= 32	
	60	$60 \div 2 = 30$

In the first instance the formula would indicate a vapor about fifteen times as heavy as hydrogen; in the second case thirty times as heavy. Experiment shows that the gas is about fifteen times as heavy as hydrogen, and therefore justifies the formula NO.

Since the introduction of a large number of atoms into a molecule does not increase the bulk occupied by a collection of such molecules, it seems reasonable to assume that the intermolecular spaces are much larger than the molecules themselves.

STOICHIOMETRY

This term (from two Greek words, which together have, figuratively, the meaning "to measure primary things") is applied to calculations of the composition of compounds and of amounts required for reactions.

The exact quantitative relations which exist in compounds, and the fact that symbols refer to definite proportions of the elements, permits the

use of the method of simple proportion to calculate the amounts involved in, or resulting from, any chemical combination. If it is required to know how much hydrogen is contained in 40 parts by weight of water, the formula expressed in quantitative ratio is as follows:—

$$\begin{aligned} H_2(2 \times 1) &= 2 \\ O &= 16 \\ H_2O &= 18 \end{aligned}$$

That is, 18 parts by weight of water contain 2 parts of hydrogen. Hence $18:2::40:x$; the fourth term will be the amount required. Percentage composition is ascertained by the same rule. The percentage of oxygen in water is obtained by the following proportion:—

$$18 : 16 : : 100 : x.$$

In ordinary calculations it is rarely necessary to use the exact fractional atomic weights. The nearest whole number will suffice. In a close calculation it would be necessary to use 1.008 as the atomic weight of hydrogen.

In the last example, the fourth term will be found to be 88.8, which is therefore the precentage required. Any chemical formula or reaction may be calculated to exact expression of weight. To determine, for instance, how much potassium iodide is required to exactly precipitate 1 gram of mercuric chloride, the reaction, that is, the equation, must first be stated. This is as follows:—

$$HgCl_2 + 2KI = 2KCl + HgI_2$$

The proportions by weights are:—

$$\begin{aligned} Hg &= 200.6 \\ Cl_2 &= 70.92 \\ HgCl_2 &= 271.52 \end{aligned} \qquad \begin{aligned} K &= 39.1 \\ I &= 126.9 \\ KI &= 166.0 \end{aligned}$$

The proportion will be, as the molecular weight of the mercuric chloride is to that of the potassium iodide with which it reacts, so is the given weight to that of the iodide required. Care must always be taken to use the molecular weights in the full proportion. In the present calculation, for instance, the molecular weight of the iodide must be doubled, because the chloride reacts with two molecules. Hence,

$$\begin{aligned} &HgCl_2 \qquad 2KI \\ &271.52 : 332(166 \times 2) : : 100 : x. \end{aligned}$$

Calculations of this character are of value to the student, who should practise them. Among other points of interest, they will serve to impress on the mind that formulas give only ratios by special factors, and do not convey directly the simple proportion. Thus, hydrogen iodide, HI, does not contain equal quantities of H and I, but only equal numbers of atoms. The calculation shows this:—

$$\begin{aligned} H &= 1 \\ I &= 126.9 \\ HI &= 127.9 \end{aligned}$$

Therefore,

$$\begin{matrix} HI & I \\ 127.9 : 126.9 :: 100 : 99.2\ \% \end{matrix} \text{ iodine;}$$

by which it is seen that hydrogen iodide contains less than 1 % of hydrogen.

CLASSIFICATION OF THE ELEMENTS

Of the few elements known in the free state in ancient times, all but sulphur and carbon were of the class now called metals. These were divided into two groups, based on the effects produced on heating them in air. Those which do not oxidize (rust) by this treatment were called *noble* metals. Those which oxidize were called *base* metals. Care must be taken not to confound this use of the word "base" (in the sense of "ignoble") with a special use of the word in modern chemistry. Of the metals known to the ancients, gold and silver were termed "noble;" lead, tin, copper and iron were termed "base." Mercury is intermediate in character, since at moderately high temperatures it is oxidized, but at still higher temperature is reconverted into pure metal. Moreover, its fluidity and solvent action on most other metals place it in a special relation. The classification into base and noble has long since been abandoned by chemists, but persisted, until comparatively recent times, in practical metallurgy; platinum and some of its associated metals were added to the first class, while the second class was very largely increased.

The first scientific classification of the elements was into *metals* and *non-metals*. The principles on which this was made are illustrated in the following synopsis of the assigned distinctions between the groups:

Metals	Non-metals
High specific gravity.	Low specific gravity.
Conduct heat and electricity readily.	Do not conduct heat and electricity readily.
High fusing points.	Low fusing points.
Mostly oxidize easily.	Do not usually oxidize easily.
Malleable and ductile.	Not malleable nor ductile.
Produce definite mixtures with each other which crystallize, but are not strictly chemical compounds.	Produce indefinite mixtures or chemical compounds.
Do not dissolve unchanged in any simple solvent.	Dissolve freely without change in many simple solvents.
Are usually in the *positive* ion of their compounds.	Are usually in the *negative* ion of their compounds.

Few elements, however, conform to either of the lists exactly. Thus, potassium and sodium have low specific gravity and low fusing points; antimony and bismuth are neither malleable nor ductile; arsenic and platinum often appear in the negative ion of their compounds; yet all of these are termed metals. Carbon, which is classified as a non-metal, has high fusing point, conducts heat and electricity readily, and is not soluble in any simple solvent.

It must be noted especially that some of the properties given in the above comparison are not properties of the atom but due to state of aggregation, that is, the manner in which the atoms are associated. Specific gravity, malleability, ductility, conducting power and even oxidability are modified by changing the physical condition. Gold can be easily converted in a dull powder which will remain long suspended in water. A correct classification must be based on the specific properties, distinctions and resemblances of the atoms. A classification into *non-metals*, *metalloids* and *metals* has been proposed, but it has no advantage.

While the classification into metals and non-metals was in general use, subdivision of the metals was made into *alkali metals*, *alkaline-earth metals* and *heavy metals;* the heavy metals being generally subdivided into *base* and *noble*. These distinctions are sometimes employed in analytical chemistry, but do not need further explanation here.

At present, classifications are based primarily on the relations of the atomic weights. Several suggestions along this line were made years ago by Döbereiner of Germany, Newlands of England, and Lea of the

PERIODIC ARRANGEMENT OF SOME IMPORTANT ELEMENTS

Zero group	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8
	Hydrogen							
Helium	Lithium		Boron	Carbon	Nitrogen	Oxygen	Fluorine	
Neon	Sodium	Magnesium	Aluminum	Silicon	Phosphorus	Sulphur	Chlorine	
Argon	Potassium	Calcium				Chromium	Manganese	Iron
								Cobalt
								Nickel
	Copper	Zinc			Arsenic	Selenium	Bromine	
Krypton	Rubidium	Strontium				Molybdenum		
	Silver	Cadmium		Tin	Antimony	Tellurium	Iodine	Ruthenium
								Rhodium
								Palladium
Xenon	Cesium	Barium						
								Osmium
								Iridium
								Platinum
	Gold	Mercury	Thallium	Lead	Bismuth			
		Radium		Thorium		Uranium		

United States, but the arrangement proposed by the Russian chemist Mendeleeff is most commonly used.

This is commonly called the "*periodic system*," because the elements are arranged in grouping "periods of eight," by means of the atomic weights, starting with the lowest weight and ending with the highest. When the list is examined as a total, it will be found that in most cases elements of similar chemical character are brought together.

The periodic system is not yet wholly satisfactory. Some elements cannot be brought into the seven-period arrangement, and are provisionally placed in extra lists. There are some gaps, but these are of less significance, because they may be filled by later discovery. In fact, since the system was first published several elements, the existence of which was indicated, have been discovered.

The table on p. 38 shows the periodic arrangement of the common elements. A few of the less common forms have been introduced on account of their practical importance in special cases.

GROUPS OF ELEMENTS

A table of known elements with symbols, and atomic weights will be found on p. 101. The following is a summary of the characteristics of some well-marked groups. Some elements have properties that ally them to several groups. They are "connecting links." Thus, fluorine connects the oxygen group with the chlorine group, boron connects the nitrogen group with the iron group, through aluminium.

1. The **Argon Group,** often called the *zero group*, on account of the apparent lack of chemical affinity, includes helium, neon, argon, krypton and xenon. They are gases, existing in minute amounts in the atmosphere. Helium occurs in some minerals and in the emanations from radium. The members of the group form, so far as is at present known, no compounds, and, therefore, the valency is zero.

2. The **Potassium Group** includes hydrogen, lithium, sodium, potassium, rubidium and cesium. They are positive monads, and have high affinity for members of the oxygen and chlorine groups. With oxygen most of them produce powerful corrosive compounds called the alkalies, and on this account are sometimes called the "alkali metals." In the periodic arrangement as usually given, copper, silver and gold are classed as an accessory sub-group. Of these three, silver shows the closest relation to the potassium group.

3. The **Calcium Group** includes calcium, barium, strontium and radium. They are positive dyads, and form oxides which are slightly soluble in water, but much less caustic or corrosive than the alkalies proper, and are often called alkaline earths. Their sulphates, carbonates and phosphates are practically insoluble in water. Magnesium, zinc, cadmium and mercury are classed as an accessory sub-group. Magnesium is closest in its resemblances to the main group. Mercury connects the group with the first group by the resemblances of copper and mercury in many of their chemical actions. Lead also has some relations to this group. In earlier classifications, the four elements, magnesium, calcium, strontium and barium constituted the group of "alkali-earth metals."

4. The **Carbon Group** includes carbon, silicon and tin. They are tetrads, and generally positive. Boron, lead and platinum have some resemblances to this group.

5. The **Nitrogen Group** includes nitrogen, phosphorus, arsenic, antimony and bismuth. They are of uneven valency, triads or pentads; their electrical relations are irregular, but mostly positive. Boron and gold have some resemblances to this group.

6. The **Oxygen Group** includes oxygen, sulphur, selenium and tellurium. They are negative dyads. Chromium, molybdenum and uranium form an accessory sub-group.

7. The **Chlorine Group** includes fluorine, chlorine, bromine and iodine. They are negative monads, and are the only elements which form salts without the aid of some member of the oxygen group. For this reason they have been called the HALOGENS, a word meaning "salt formers." Manganese is placed here as in some ways analogous to the group, but its most striking relations are with iron.

8. The **Iron Group** is positive, and includes iron, nickel, cobalt and probably several other elements the chemistry of which is not well known. They are not found in the metallic state, except in small quantity. Most of them form two sets of compounds, acting in one as dyads, in the other as double tetrads. Several form well marked acid anhydrides. Manganese, chromium and aluminum have so many chemical relations with the iron group that they are more conveniently described with it.

This system of classification will not be rigidly followed in the description of the elements and their compounds; the most important substances will be described out of the regular order.

In the description of the elements, the atomic weights are given to the nearest first decimal or when this is small, to the nearest whole number. The closer figures will be found in the table on p. 101.

Atomic Number.—About a dozen years ago, a British scientist, Moseley, by examining elements with *x*-rays found that effects are obtained which enable the whole list to be arranged in numerical order by increasing atomic weights, except in a few cases in which a lower weight follows a higher. These exceptions are not regarded as important. The result of Moseley's work was to show also that a few numbers are without any assigned element. This suggested that the gaps were due to elements as yet undiscovered and stimulated research. The suggestion has been confirmed and within a few years all but two of the missing elements have been found. 43, 61, 71, 75, 85, 87 and 91 were lacking at first. Moseley lost his life in the British service in the Dardenelles during the world war.

The following is a list of atomic numbers as at present arranged

1 H	20 Ca	39 Yt	58 Ce	77 Ir
2 He	21 Sc	40 Zr	59 Pr	78 Pt
3 Li	22 Ti	41 Nb	60 Nd	79 Au
4 Gl	23 V	42 Mo	61 Il	80 Hg
5 B	24 Cr	43 Ma	62 Sa	81 Tl
6 C	25 Mn	44 Ru	63 Eu	82 Pb
7 N	26 Fe	45 Rh	64 Gd	83 Bi
8 O	27 Co	46 Pd	65 Tb	84 Po
9 F	28 Ni	47 Ag	66 Dy	85
10 Ne	29 Cu	48 Cd	67 Ho	86 Rd
11 Na	30 Zn	49 In	68 Er	87
12 Mg	31 Ga	50 Sn	69 Tm	88 Ra
13 Al	32 Ge	51 Sb	70 Yb	89 Ac
14 Si	33 As	52 Te	71 Lu	90 Th
15 P	34 Se	53 I	72 Hf	91 Pa
16 S	35 Br	54 Xe	73 Ta	92 U
17 Cl	36 Kr	55 Cs	74 W	
18 A	37 Rb	56 Ba	75 Re	
19 K	38 Sr	57 La	76 Os	

85 and 87 remain to be discovered. The former will belong to the chlorine group and the latter to the potassium group.

DESCRIPTIVE INORGANIC CHEMISTRY

HYDROGEN

Hydrogen, H, I (more closely 1.0075), exists in water and all organic substances.

It is prepared by the action of electricity on water or dilute acids; also by the action of some elements on water or acids. With acids, the action generally occurs without the aid of heat; with water, sodium and potassium act in the cold; iron, magnesium and zinc require a high temperature.

$$Na + H_2O \rightarrow NaHO + H.$$
$$Mg + H_2O \rightarrow MgO + H_2.$$
$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2.$$

The last method is that generally used in the laboratory.

Hydrogen is also evolved readily by the action of sodium hydroxide on aluminum.

$$Al + 3NaHO \rightarrow Na_3AlO_3 + H_3.$$

Na_3AlO_3 is usually called sodium aluminate.

The action of steam on iron gives hydrogen by a reversible reaction (p. 20) since if hydrogen is passed over iron oxide water is formed and iron set free.

Pure hydrogen is a colorless, tasteless and odorless gas. It is the lightest body known, a liter weighing 0.08961 gram. 100 cubic inches weigh 2.14 grains. It will burn in air or oxygen, forming water. Hydrogen, though not poisonous, will not sustain life; small quantities, when pure, can be inhaled without apparent injury.

By intense cold and pressure, hydrogen is condensed to a colorless liquid, much lighter than water.

Hydrogen is a positive monad, and a standard for valency, atomic and molecular weight and density. It combines with many elements. It is the essential element of acids. It is a feeble reducing agent at ordinary temperatures, but at high temperatures is active. It is also an active reducing agent in the nascent state.

OXYGEN

Oxygen, O, 16.—This exists in water, air, all animal and vegetable tissues and in most of minerals. It constitutes over half the matter composing the earth.

Several oxides are decomposed by heating. The decomposition of mercuric oxide in this manner was the means of the discovery of the gas. The reaction is reversible (p. 19) since at a moderate temperature the mercury is oxidized and at a higher temperature the oxygen is expelled. Hence it is written

$$Hg + O \rightleftarrows HgO.$$

Chlorates and nitrates are decomposed by heat, giving off large quantities of oxygen, but not always quite pure. Potassium chlorate mixed with about one-quarter of its weight of manganese dioxide is preferred.

The reaction concerns the potassium chlorate only, which is decomposed as follows:—

$$KClO_3 \rightarrow KCl + O_3.$$

The exact manner in which manganese dioxide acts is not known. It is an instance of catalysis (see p. 21).

Oxygen is colorless, odorless and tasteless; it is one-tenth heavier than air, 1 liter weighing 1.43 grams. It is continually being absorbed by living animals in the process of respiration, to which function it is essential, and is also consumed in ordinary combustion. All bodies which burn in air burn with increased brilliancy and rapidity in pure oxygen.

Plants under the influence of light both excrete and absorb oxygen. The *absorption* of oxygen by plants is a process of respiration, and takes place during the whole life of the plant; the *excretion* of oxygen is dependent on a process of feeding, and takes place only when the plant is exposed to light.

Oxygen combines with every other element except fluorine and the members of the argon group, and with many in several proportions. The chemical functions of these oxides are dependent in part upon the number of oxygen atoms present. Those of manganese may be taken as examples:—

MnO	Powerful base.
Mn_2O_3	Weak base.
MnO_2	Indifferent.
MnO_3	Forming an acid (anhydride).

These illustrate the law that small proportions of oxygen tend to produce bases, high proportions anhydrides or acid-forming oxides, and intermediate proportions bodies of uncertain or indifferent character. Elements of intermediate electrical character are incapable of forming basic oxides. Thus, nitrogen forms five oxides; none of them has basic powers, but several form powerful acids.

Oxygen is slightly soluble in water, and upon this fact depends the existence of most forms of aquatic life.

The removal of oxygen from any compound is called *reduction;* the addition of oxygen is called *oxidation.* Substances which bring about the former action are called *reducing* agents, those causing the latter effect, *oxidizing* agents. These terms are now extended to actions involving the removal or addition of other negative elements. Thus the conversion of ferric chloride into ferrous is called a reduction, and the reverse operation (ferrous chloride into ferric) is called an oxidation.

Oxygen can be liquefied by intense cold and pressure. The liquid is light blue, boils at $-181°$ C. ($-358°$ F.). At the boiling point it is heavier than water.

Ozone.—Ozone is a modified form of oxygen in which three atoms constitute a molecule. The contrast between the conditions is shown thus:—

Ordinary oxygen

$$O = O$$

Ozone

Ozone may be prepared by passing electrical sparks through air or oxygen; by the slow oxidation of phosphorus or of turpentine, or other essential oils; by the decomposition of water by electricity; by the action of acids upon certain bodies rich in oxygen. By all these methods only a small proportion of the oxygen is converted into ozone. When barium dioxide or potassium permanganate is mixed with strong sulphuric acid, some ozone forms.

Ozone is heavier than oxygen.

When the properties of an element are modified without alteration of composition, the change is said to be *allotropic.* Ozone is an allotropic form of oxygen.

WATER

When two volumes of hydrogen and one volume of oxygen are combined, complete condensation takes place and water is formed.

Water, H_2O, exists abundantly, not only collected in masses, as in rivers, lakes and seas, but in combination with many substances and in a state of mixture with inorganic and organic bodies. Air almost always contains some water. Some living structures, as succulent fruits and jelly fish, consist almost entirely of water. In natural conditions water is never pure. The materials dissolved range ordinarily from 5 to 30 grains to the gallon. When the quantity greatly exceeds this, and especially when peculiar substances, such as iron or sulphides, are present, it constitutes a mineral water. Sea water is very rich in mineral substances.

The most important varieties of mineral waters are—

Alkaline or carbonated waters, containing various carbonates in solution, generally with a quantity of carbonic acid.

Chalybeate waters, containing iron, generally as ferrous carbonate, with carbonic acid.

Sulphur waters, containing hydrogen sulphide and other sulphides.

Acid waters, containing some of the stronger acids.

Saline or aperient waters, having large amounts of chlorides and sulphates.

Water combines with many bodies. There are two principal classes of these compounds. In one class, the water seems to unite as such with the other substance; in the other class, the molecule of water is broken up.

Of the first kind of combination instances are seen in common crystals. The blue crystals sold as copper sulphate contain $CuSO_4$, $5H_2O$. Water, that is in this way part of a molecule and has some influence on the crystalline form, is often called WATER OF CRYSTALLIZATION. Substances that do not contain water of crystallization or which have been deprived of it, are said to be ANHYDROUS. Water of crystallization is usually easily driven out by heat.

The second form of the chemical action of water is seen when water is mixed with quicklime; a violent action ensues, and the compound CaH_2O_2 results. A considerable number of oxides are capable of uniting thus with water and forming bodies known as hydroxides. This action of water is termed *hydrolysis*. It will be specially studied in connection with organic chemistry.

The oxides which, by addition of water, produce hydroxides are called ANHYDRIDES. By subtracting H_2O from any hydroxide the corresponding anhydride is obtained. Acids in this way furnish anhydrides:—

Sulphuric acid — Sulphuric anhydride

$$H_2SO_4 - H_2O \rightarrow SO_3.$$

If the acid contains but one atom of hydrogen, the formula must, of course, be doubled before subtracting. Hence—

Nitric acid — Nitric anhydride

$$2HNO_3 - H_2O \rightarrow N_2O_5.$$

The term anhydride generally refers to those bodies which yield acids by addition of water. Those which yield hydroxides capable of neutralizing acids are generally called bases.

Water is the most powerful ionizing liquid known. It promotes chemical action in many ways. For the study of electric conductivities, now a very important phase of research, water of high purity is needed. It is made by distillation in quartz vessels, and is known as "conductivity water."

HYDROGEN PEROXIDE

Hydrogen peroxide H_2O_2, often called *hydrogen dioxide* and sometimes *oxygenated water*, is obtained when oxygen is liberated in presence of water. When dilute acids are decomposed by a current of electricity, a small amount of the peroxide forms at the positive pole. The best method of preparing it is by decomposing some oxides in presence of large amount of water. When barium peroxide is mixed in the cold with very dilute acids the following reaction occurs (sulphuric acid being taken as an example):—

$$BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2.$$

The presence of a considerable excess of water is necessary to the success of this reaction. Dilute solution of hydrogen peroxide can be conveniently prepared by dissolving sodium peroxide in dilute acid. Pure hydrogen peroxide is a colorless, odorless, bitter, transparent, oily liquid, nearly one-half heavier than water. It blisters the skin and bleaches organic colors. It is decomposed by heat and by many chemical substances, often explosively. The preparation of the concentrated liquid is difficult, but a dilute solution can be easily kept, and is now a commercial article, being used for bleaching hair, and as a disinfecting and oxidizing agent.

The strength of the commercial solutions of hydrogen peroxide is usually expressed by the amount of oxygen that will be given off in decomposition by the reaction $H_2O_2 \rightarrow H_2O + O$. This is termed the "available

oxygen." A solution containing 3 % by weight of hydrogen peroxide will yield by this reaction about ten volumes of oxygen, that is, 100 c.c. of such a solution (containing 3 grams of the peroxide) will yield about 1000 c.c. of oxygen. Hence, this is termed a *ten-volume* solution. A *twenty volume* solution would correspond to 6 %. H_2O_2. The standard commercial strength is ten volumes (3 % H_2O_2). Potassium permanganate and hydrogen peroxide decompose each other. The experiment is best carried in presence of dilute sulphuric acid, when the following reaction occurs:—

$$5H_2O_2 + K_2Mn_2O_8 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + O_{10}.$$

The amount of oxygen liberated is double that in the hydrogen dioxide. The reaction is exact enough to be applicable as a method of assaying samples.

Dilute, slightly acid, solutions of hydrogen peroxide keep very well, but a neutral solution does not and alkaline solutions quickly decompose. Hydrogen peroxide decomposes quickly when brought in contact with pus, the liberated oxygen causing the mixture to foam.

CHLORINE

Chlorine, Cl, 35.5.—The most abundant compound is common salt, NaCl. Many other chlorides are found as minerals.

Several methods for the preparation of chlorine have been devised; nearly all of them depend upon the oxidation of some chloride.

(*a*) By heating a mixture of manganese dioxide and hydrochloric acid:—

$$MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2.$$

(*b*) By heating a mixture of common salt, sulphuric acid and manganese dioxide:—

$$MnO_2 + 2NaCl + 2H_2SO_4 \rightarrow MnSO_4 + Na_2SO_4 + 2H_2O + Cl_2.$$

(*c*) By the action of hydrochloric acid upon potassium chlorate, potassium dichromate or bleaching powder. These methods yield an impure chlorine, but are suitable for the preparation of small amounts.

The reaction with potassium chlorate may be represented as follows:—

$$2KClO_3 + 4HCl \rightarrow 2KCl + Cl_2O_4 + Cl_2 + 2H_2O.$$

Chlorine is a greenish-yellow, highly irritating gas. It can be condensed to a greenish liquid by moderate cold and pressure. The gas is about two and a half times as heavy as air; 1 liter weighs 3.18 grams; water

dissolves about three volumes, acquiring the color and odor of the gas; the solution, known as *chlorine water*, does not keep well.

The affinities of chlorine are very great. It combines directly with most of the metals, decomposes water, and changes many organic substances. Its affinity for hydrogen is increased by light.

It has many applications as a bleaching and disinfecting agent, but is rarely used in the form of gas, the effects being generally obtained by the use of *bleaching powder* (see hypochlorites).

Chlorine is a monad in its strictly negative relations, *i. e.*, in simple chlorides, but in association with oxygen, it assumes higher valencies. It is also capable of replacing hydrogen, atom for atom, giving rise to an important and extensive series of *substitution* compounds, which are considered in connection with organic chemistry.

Hydrochloric Acid, HCl, *Muriatic Acid, Spirit of Salt.*—This acid may be formed by the direct union of its elements, but the practical process is the reaction of common salt and sulphuric acid, according to the following equation:—

$$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl.$$

This reaction requires a high temperature. In ordinary experiments and on the small scale the reaction is—

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl.$$

Hydrochloric acid is a colorless gas of a strong pungent odor and poisonous to animals and plants. Its density is 18.18; a liter weighs 1.63 grams. It does not burn nor support ordinary combustion, but some substances burn in it, forming chlorides. Water will absorb nearly 500 volumes, producing a strongly acid solution, which is the common hydrochloric or muriatic acid. When pure this is a colorless, fuming, strongly acid liquid.

Many metals dissolve in hydrochloric acid, forming chlorides and liberating hydrogen; oxides dissolve, forming chlorides and water, sulphides form hydrogen sulphides. The following reactions illustrate this:—

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2.$$
$$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O.$$
$$FeS + 2HCl \rightarrow FeCl_2 + H_2S.$$

With many oxides, some chlorine escapes as in the reaction with manganese dioxide or lead dioxide.

$$MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2.$$

A mixture of about three parts nitric with five parts hydrochloric acid has been long used under the names *aqua regia* and *nitro-muriatic acid*. It dissolves gold and platinum, owing its efficacy in part to the free chlorine which is formed by the oxidizing of the nitric acid upon the hydrochloric acid.

Compounds of Chlorine and Oxygen.—Several of these are known in the free state. Others are known only in combination, as in the following series:—

$HClO$	Hypochlorous acid.	H—O—Cl.
$HClO_2$	Chlorous "	H—O—ClO_2.
$HClO_3$	Chloric "	H—O—ClO_2.
$HClO_4$	Perchloric "	H—O—ClO_3.

Any positive may take the place of the hydrogen, forming a salt.

Chloric Acid, $HClO_3$.—When chlorine acts upon metallic oxides or hydroxides at a temperature of over 15.5° C. (60° F.) *chlorates* will be produced, according to the following reaction:—

$$6KHO + Cl_6 \rightarrow KClO_3 + 5KCl + 3H_2O.$$

The chlorates are useful for the large amount of oxygen which they contain, and which they yield when heated. Potassium chlorate is the substance from which oxygen is usually prepared. Perchloric acid is obtained by heating dilute chloric acid. The perchlorates resemble the chlorates.

When chlorine acts upon hydroxides, at a low temperature, hypochlorites are produced. (See calcium hypochlorite.) A weak solution of hypochlorous acid is sometimes used for removing ink.

Chlorine combines with nitrogen to form nitrogen chloride. It is an oily liquid, which decomposes very easily and with violent explosion.

BROMINE

Bromines, Br, 80.—Bromides occur in sea water, sea plants, brine springs and in a few minerals. Bromine may be prepared by processes analogous to those of chlorine—acting upon bromides by means of oxidizing agents, such as a mixture of sulphuric acid and manganese dioxide:—

$$2KBr + MnO_2 + 2H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + 2H_2O + Br_2.$$

It may also be directly expelled by the superior affinity of chlorine:—

$$KBr + Cl \rightarrow KCl + Br.$$

Bromine is a dark red liquid, which at ordinary temperatures evolves irritating red vapors. It is about three times as heavy as water, boils at 145° F. (63° C.) and freezes at −12° F. (−25° C.). It is soluble in water, and is often conveniently used in that form. Its chemical properties are similar to those of chlorine, but not so energetic. It bleaches vegetable colors and decomposes many organic substances.

It combines energetically, forming bromides, of which those from hydrogen, potassium and ammonium are the most important. It also forms oxygen compounds analogous to those of chlorine.

Hydrogen Bromide, Hydrobromic Acid, HBr.—This substance cannot be conveniently prepared by the action of sulphuric acid upon a bromide, but is obtained by using a mixture of phosphorus, powdered glass and bromine, or by the action of phosphoric acid upon a bromide. It resembles hydrochloric acid in its properties, and is used in medicine.

Bromic Acid, $HBrO_3$, which forms bromates, and *Hypobromous Acid*, HBrO, which forms hypobromites, are also known. They resemble the corresponding chlorine compounds.

IODINE

Iodine, I, 127.—Iodides occur in association with bromides and chlorides in sea water and sea plants.

Iodine is prepared from any iodide, by processes similar to those for bromine, either by the action of chlorine or of a mixture of manganese dioxide and sulphuric acid. The reactions are—

$$KI + Cl \rightarrow KCl + I,$$

or,

$$2KI + MnO_2 + 2H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + 2H_2O + I_2.$$

It forms bluish-black crystalline masses with metallic luster. It evaporates slowly at ordinary temperatures, melts at 225° F. (107° C.), and boils at 347° F. (175° C.). The vapor is blue-violet and of a peculiar odor, somewhat like that of chlorine, but is not so irritating. The solid dissolves freely in alcohol, ether and carbon disulphide; also in water containing potassium iodide, but only slightly in pure water. It has some bleaching, oxidizing and disinfecting powers. An important property of iodine is the production of a blue color with starch. The iodine must be in the free state; iodides give no color.

The chemical relations of iodine are substantially the same as those of chlorine and bromine.

Hydrogen Iodide, HI, *Hydriodic Acid*.—This is prepared by methods similar to those used for hydrogen bromide, which body it closely resembles. It is used in medicine.

By the action of strong ammonium hydroxide upon powdered iodine a brownish substance is produced, having probably the composition NHI_2. It is easily handled while wet, but when perfectly dry it explodes, with a loud report, on the slightest touch.

FLUORINE

Fluorine, F, 19.—This is tolerably abundant in fluor spar, CaF_2, and cryolite, $3NaF,AlF_3$, and some rarer minerals. It exists in the stems of grasses and in bones and teeth.

Fluorine is a gas. It combines with every active element except oxygen. When perfectly dry it has not very high affinity, but a small amount of moisture causes it to act on many substances. It has a high affinity for silicon.

Hydrogen Fluoride, *Hydrofluoric Acid*, HF.—This body is prepared by acting on calcium fluoride, CaF_2, with sulphuric acid. The pure acid is a gas, but will dissolve in water. It acts powerfully, especially on siliceous materials, *e. g.*, glass, clay, granitic rocks. It is used for etching designs on glass.

Strong solution of hydrogen fluoride is now sold in gutta percha or paraffin bottles, upon which it has no action. It is much used in the analysis of minerals. The acid and the soluble fluorides are strong antiseptics.

NITROGEN

Nitrogen, N, 14, constitutes about four-fifths of air, and occurs in many animal and vegetable tissues, also as sodium and potassium nitrates.

It is a gas without color, taste or smell. It does not burn or support combustion, and is not poisonous, but will not support life. At high temperature, and also under the influence of electric discharges, it will enter into combination with oxygen, boron, silicon, carbon, hydrogen, and magnesium. It is a little lighter than air; a liter weighs 1.25 grams. It can be liquefied by intense cold and pressure. There is an allotropic more active form.

Nitrogen is generally a pentad; sometimes it acts as a triad, or even as a monad. It is an essential ingredient of all the higher tissues of animals, and exists also in vegetable structures, but not so abundantly.

Most of the powerful explosives now in use—gun cotton, nitro-*glycerin*, and TNT, for instance—owe their qualities largely to the nitrogen present.

Air.—The atmosphere is an intimate *mixture* of about four volumes of nitrogen with one volume of oxygen. It surrounds the earth to the height of many miles. Air is dissolved by water, but the nitrogen and oxygen are in proportion different from that in ordinary air. The composition of air is not absolutely constant nor in exact atomic proportions, either by weight or volume.

That the composition of air varies so little is due to the fact that all gases mingle with one another, so that sooner or later they produce a uniform mixture in spite of the influence of gravity. The rate of mixture depends on the density of the gas.

Ordinary air contains small quantities of other substances besides nitrogen and oxygen. It always contains water, carbonic acid, and ammonia, with small amounts of the elements of the argon group; frequently ozone and compounds of nitrogen and oxygen. Dust and the products of animal and vegetable decomposition are accessory impurities. The study of impurities of air has received much attention of late years, especially in view of the fact that many diseases are due to living organisms, or germs which are conveyed in the air.

The following may be taken as an average composition, as far as the abundant constituents are concerned:—

Oxygen	20.61
Nitrogen	77.95
Carbon dioxide	0.03
Water	variable

100 cubic inches of air weigh 30.93 grains; 1 liter weighs 1.29 grams; 13 cubic feet weigh about 1 pound. At the level of the sea the pressure is, ordinarily, about 15 pounds per square inch, and will sustain a column of mercury 760 millimeters, or 30 inches, in height. Water in its natural condition always contains some air in solution.

The capacity of air for holding moisture increases rapidly as the temperature rises. The dryness or dampness of the atmosphere is not due to the actual quantity of moisture in it, but to the amount present in proportion to that which the air can take up. The nearness of air to saturation is called the *relative humidity*. Air saturated with water

has a relative humidity of 100; if half saturated, the relative humidity is 50, and so on. When the temperature falls the moisture separates to a greater or less extent, and produces fog, rain, or dew, and if the temperature gets below the freezing point, snow or frost.

The respiration of animals and the processes of combination and decay are continually changing the air, by removing oxygen and introducing water, carbonic acid, organic matter, ammonia, and hydrogen sulphide. Dust floating in the air contains substances living and dead, and varies with the locality. The continued removal of oxygen is partially counterbalanced by the action of plants, which, under the influence of light, decompose the carbonic acid, retaining the carbon and giving off the oxygen, especially at the under surface of the leaves. Plants also absorb oxygen and excrete carbon dioxide continuously; this process not depending on light. The nitrogen of the atmosphere is somewhat affected in these actions. Ammonia and other gases are gradually oxidized or absorbed by the soil and plants and washed out by the rains. The organic matter is also oxidized.

Ammonia, NH_3, *Ammonia Gas*.—This is given off in the decomposition of organic matter, especially animal remains, and was originally derived from refuse of this kind. It is also produced by the action of hydrogen on nitric acid. For many years the principal source was the water used for washing illuminating gas, but at present the manufacture by the fixation of the nitrogen of the air is operated on a very large scale. Three methods have been exploited,

(1) Passing air over an electric spark, by which nitrogen oxides are formed which can be converted into nitric acid and ammonia.

(2) Action of nitrogen on calcium carbide by which calcium cyanamide, $CaCN_2$, is formed. This can be used directly as a fertilizer or converted into ammonia or other nitrogen compounds.

(3) The most important method and one which has been operated on a very large scale in the last dozen years, is the direct union of nitrogen and hydrogen. This has been developed especially by a German chemist, Haber, under whose plans plants of very large output were operated in Germany during the war. The process requires high heat, high pressure and the influence of a catalyst. Its operation rendered Germany independent of the importation of nitrates from Chile during the war, as the nitric acid needed for explosives can be prepared from ammonia. The problem of nitrogen fixation is of the greatest moment in view of the possible early exhaustion of the supply of nitrates in Chile.

Ammonia may be obtained by heating a mixture of ammonium chloride (NH_4Cl) and lime:—

$$2NH_4Cl + CaO \rightarrow 2NH_3 + H_2O + CaCl_2.$$

By passing the gas over dry lime the water is absorbed and the pure gas is collected.

Ammonia (which might with advantage be called "amine") is a colorless gas of a pungent odor. It is absorbed in large amounts by water, 1 pint absorbing 700 pints of gas and increasing 50 % in volume. This solution exhibits most of the properties of the gas, and is much used under the name of *aqua ammoniæ* or solution of ammonia.

Ammonia is lighter than air. 1 liter weighs 0.76 gram. At a temperature of −40° F. (−40° C.), or under a pressure of 100 pounds to the square inch, it condenses to a colorless liquid. This liquid evaporates rapidly when the pressure is removed, and produces great cold, which fact has been made use of in machines for making ice.

The solution of ammonia in water has strongly alkaline and basic powers, resembling potassium hydroxide and sodium hydroxide. It has received the name of *volatile alkali*, the others being called fixed alkalies. The compounds produced by it may be formulated in the same manner as those of potassium and sodium, these elements being represented by the radical, NH_4. In this way $NH_3 + HCl$ would produce NH_4Cl; $NH_3 + H_2O$ would produce NH_4HO. NH_4 is a radical called *ammonium;* its valency is one; it combines with one atom of chlorine and can replace the hydrogen of acids.

The following formulas show the comparison between the salts of potassium and those of ammonium:—

KCl	Potassium chloride.
NH_4Cl	Ammonium chloride.
K_2SO_4	Potassium sulphate.
$(NH_4)_2SO_4$	Ammonium sulphate.
KNO_3	Potassium nitrate.
NH_4NO_3	Ammonium nitrate.
KHO	Potassium hydroxide.
NH_4HO	Ammonium hydroxide.

The important compounds of ammonium are described in connection with those of potassium and sodium, which they resemble in many respects in properties and uses.

Nitrogen Oxides.—Five compounds of nitrogen and oxygen have been obtained:—

N_2O	Nitrous oxide, laughing gas.
NO	Nitric oxide (often written N_2O_2).
N_2O_3	Nitrous anhydride.
NO_2	Nitrogen dioxide (often written N_2O_4).
N_2O_5	Nitric anhydride.

The names of these compounds are confused. Thus, NO is often written N_2O_2, and called nitrogen dioxide. NO_2 is written N_2O_4, and called nitrogen tetroxide.

Nitric Acid, Aqua fortis, HNO_3, is made by the action of strong sulphuric acid upon nitrates. The reaction with sodium nitrate is—

$$2NaNO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2HNO_3.$$

Nitric acid thus obtained has the composition HNO_3; when quite pure it is colorless but is liable to decomposition, and is dangerous to use. It is sometimes called "fuming" nitric acid. The common commercial acid contains much water. It is a strongly acid liquid, highly corrosive and poisonous and of high oxidizing power. Only part of the oxygen of the acid is available. The effect is in most cases represented thus:—

$2HNO_3$ decomposes into $H_2O + 2NO + O_3$.

The O_3 is the available oxygen. With some bodies the acid acts simply by exchanging its hydrogen. Thus:—

$$Zn + 2HNO_3 \rightarrow Zn(NO_3)_2 + H_2.$$

The nascent hydrogen, however, usually attacks another portion of nitric acid and forms ammonium nitrate, by the following equation:—

$$2HNO_3 + H_8 \rightarrow 3H_2O + NH_4NO_3.$$

In consequence of this reaction, if a few drops of nitric acid are added to a mixture of zinc and sulphuric acid, the evolution of hydrogen will not be increased but diminished; the hydrogen liberated by the action of the zinc on the sulphuric acid is at once taken up without appearing in the free state and ammonium nitrate formed.

If basic oxides are formed by the oxidizing action of nitric acid, they will unite with another portion of the acid to form nitrates. In the case of copper, the following reactions take place:—

Oxidation of the copper occurs first—

$$Cu_3 + 2HNO_3 \rightarrow 3CuO + H_2O + 2NO.$$

The CuO then acts upon other nitric acid—

$$2CuO + 6HNO_3 \rightarrow 3Cu(NO_3)_2 + 3H_2O.$$

The complete reaction is, therefore—

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO.$$

Tin gives the following:—

$$Sn_3 + 4HNO_3 \rightarrow 3SnO_2 + 2H_2O + 4NO.$$

SnO_2 is not basic, and therefore does not form a nitrate, as copper oxide would. Instead of this it takes water and forms an acid.

Many organic bodies are oxidized by nitric acid.

Another action of nitric acid is in forming substitution compounds. When benzene, C_6H_6, is treated with strong nitric acid, one atom of hydrogen is removed and one molecule of NO_2 put in its place. For instance:—

$$C_6H_6 + HNO_3 \rightarrow C_6H_5(NO_2) + H_2O.$$

The body so formed is called *Nitrobenzene.*

A mixture of nitric and sulphuric acids is often used for such effects.

Very strong nitric acid fails to act upon some substances which are readily attached by the dilute forms.

The strong acid produces yellow stains on organic matter.

Nitrous Oxide, N_2O, *laughing gas*, sometimes called *nitrogen monoxide*, is obtained from ammonium nitrate, which, when carefully heated, decomposes completely into nitrous oxide and water:—

$$NH_4NO_3 \rightarrow N_2O + 2H_2O.$$

It is a colorless, odorless, somewhat sweetish gas. It supports combustion. At a pressure of fifty atmospheres, it becomes a colorless liquid, and is now sold in this form in strong metal cylinders. Nitrous oxide may be regarded as the anhydride of hyponitrous acid, HNO, several derivatives of which have been obtained. When inhaled freely, a short insensibility is produced.

Nitric Oxide, NO, often called nitrogen dioxide and written N_2O_2, is a frequent product of the action of nitric acid. Thus, with copper the reaction is—

$$Cu_2 + 8HNO_2 \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO.$$

Some N_2O, by a more extensive reduction of the nitric acid, is often produced in this experiment.

NO is a colorless gas, but when brought in contact with oxygen it instantly absorbs one atom, becoming NO_2 and turns brownish-red.

Nitrogen Dioxide, NO_2, *Nitrogen Peroxide.*—These names are owing to uncertainty in the chemical relations of the body. It has also been called nitrogen tetroxide (being written N_2O_4) and hyponitric acid, and by other less common names. The proper name is nitrogen dioxide, to correspond to the formula NO_2. It is a brownish-red gas, easily condensed to the liquid form and readily absorbed by water.

Nitrous anhydride, N_2O_3, and nitric anhydride, N_2O_5, are unimportant, as is also nitrous acid, HNO_2. Nitrities are frequently found in small amount in well water.

SULPHUR

Sulphur, S, 32, occurs native—*i. e.*, in the free state; also in combination, forming sulphides and sulphates, and in some animal and vegetable structures.

It is seen in several forms; *roll sulphur or brimstone*, made by casting the melted sulphur in moulds; *flowers of sulphur*, made by condensing the distilled sulphur in a cool chamber, and *precipitated sulphur*, a finely divided medicinal form, prepared by precipitation.

Ordinarily, sulphur is a brittle, yellow solid, insoluble in water, highly combustible, fusible at about 250° F. (121° C.) and boiling at 836° F. (447° C.). It is a non-conductor of electricity, and becomes highly electrical by friction. It assumes several allotropic forms, among which is a somewhat plastic mass, made by rapidly cooling melted sulphur. This is not permanent; it soon changes to the ordinary form.

Like oxygen, sulphur combines directly, when heated, with many metals. In these compounds it is negative, and usually dyad. With the members of its own group it combines in several proportions, showing valencies of two, four and six, and perhaps even higher. In combination with oxygen and chlorine, it is regarded as positive to them. In general its compounds are analogous in composition to those of oxygen, and since many oxides act as bases toward the ordinary acids, so the corresponding sulphides act as bases toward what are called the sulphur acids. In such compounds the sulphur is substituted for the oxygen, atom for atom, and the name is formed by prefixing either the syllable "*sulph*" or "*thio*" to the name of the acid. The latter prefix is now preferred. Thus we have—

$K_2O + CO_2 \rightarrow K_2CO_3$ ..... Potassium carbonate.
$K_2S + CS_2 \rightarrow K_2CS_3$ ..... Potassium thiocarbonate.

Sulphur is used in the arts for vulcanizing caoutchouc and in the manufacture of gunpowder.

Sulphur forms two compounds with hydrogen:—

H_2S..... Hydrogen sulphide.
H_2S_2..... Hydrogen disulphide.

Hydrogen Sulphide, H_2S.—This substance is a gas. It exists in solution in some spring waters, also in the emanations from decomposing animal and vegetable matters. It may be made by acting upon sulphides with strong acids. Ferrous sulphide and sulphuric acid are used:—

$$FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S.$$

Hydrogen sulphide may also be obtained by heating a mixture of hydrochloric acid and antimony sulphide:—

$$Sb_2S_3 + 6HCl \rightarrow 2SbCl_3 + 3H_2S.$$

It is a colorless gas, of disagreeable odor, and easily combustible. Water at ordinary temperature dissolves about three volumes, acquiring the odor and chemical properties of the gas. The important property of hydrogen sulphide is its power of precipitating many elements as sulphides. These precipitates being generally distinct in color and highly insoluble, their production is not only a test for the presence of such bodies, but also a means of separating them from solution.

Hydrogen Persulphide, H_2S_2.—This substance is a yellow oily liquid, of a disagreeable odor, decomposing easily, and is analogous to hydrogen peroxide.

Compounds of Sulphur with Oxygen.—Sulphur forms with oxygen a number of acid-forming oxides or anhydrides, some of which are known only in the hydroxide condition—that is, as acids. The important ones are:—

Anhydride	Acid	Name
SO	H_2SO_2	Hyposulphurous.
SO_2	H_2SO_3	Sulphurous.
SO_3	H_2SO_4	Sulphuric.
	$H_2S_2O_3$	Thiosulphuric.

Sodium thiosulphate is commonly called sodium hyposulphite but Na_2SO_2 is true hyposulphite. A compound, $Na_2S_2O_4$, has been introduced into industrial use of late years. It is generally called sodium hydrosulphite, but some times sodium hyposulphite. The latter name is entirely

inappropriate, and the former unsatisfactory. Sulphur forms a number of compounds that are not analogous to those of its allied elements.

Sulphur Dioxide Sulphurous Anhydride, SO_2.—This is the usual product of the burning of sulphur or the sulphides in air or in oxygen. It may also be obtained by deoxidizing sulphuric acid with copper, mercury, charcoal, silver or sulphur.

The reaction in the preparation of it by the action of sulphuric acid on copper is—

$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + 2H_2O + SO_2.$$

Mercury and silver also give similar reactions. Carbon and sulphur act as follows:—

$$C + 2H_2SO_4 \rightarrow 2SO_2 + 2H_2O + CO_2.$$
$$S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O.$$

Sulphur dioxide can also be obtained by the action of ordinary acids on sulphites.

It is a colorless gas, very irritating to the mucous membranes of the nose and throat. It can easily be condensed to a colorless liquid by a mixture of snow and salt. The liquid is sulphur dioxide, SO_2, and not sulphurous acid. In water it forms sulphurous acid, $H_2O + SO_2 \rightarrow H_2SO_3$, which remains in solution, giving the liquid all the common properties of an acid. The solution is also a powerful reducing agent, and has moderate bleaching power. It slowly becomes converted into sulphuric acid by exposure to air.

The anhydride, free acid and its salts are antiseptic, disinfectant and germicidal.

The salts of sulphurous acid are called sulphites; monads form two compounds, acid and normal. Thus, potassium gives—

Acid potassium sulphite	Potassium sulphide
$KHSO_3$.	K_2SO_3.

Dyads give one sulphite. Calcium yields $CaSO_3$.

Sulphur, Trioxide, Sulphuric Anhydride, SO_3, is a soft, white, odorless solid, in long, silky crystals like asbestos. Exposed to the air, it absorbs water rapidly and becomes converted into sulphuric acid.

Sulphuric Acid, H_2SO_4 $(HO)_2SO_2$, *oil of vitriol*, occurs in waters of volcanic and mining districts, and in the air of towns, in the latter case derived from the oxidation of sulphurous acid. The compounds of sulphuric acid (sulphates) are of frequent occurrence. Calcium and barium

sulphates are abundant minerals; sodium sulphate occurs in many natural waters.

Sulphuric acid was originally prepared by distilling ferrous sulphate. This process yields a heavy oily liquid, now commonly called *Nordhausen or fuming sulphuric acid.*

Commercial sulphuric acid was for many years made by what is termed "the leaden chamber method." In a large room, lined completely with lead (to resist corrosion), sulphur dioxide, water and vapors of nitric acid are mixed. The nitric acid oxidizes the dioxide to teroxide (sulphuric anhydride) and the water converts it into sulphuric acid. By admission of air, the reduced nitric acid is partially re-oxidized, and can oxidize more sulphur dioxide. The process can be repeated many times, hence a small amount of nitric acid will oxidize much sulphur dioxide. The action is not termed catalytic. The sulphur dioxide is obtained by the burning of native sulphur or roasting of pyrites.

$$S + O_2 \rightarrow SO_2.$$

A more economic process is dependent on the fact that when a mixture of sulphur dioxide and air is passed over hot platinum sponge (see under "Platinum") a continuous combination will take place, sulphuric anhydride being formed.

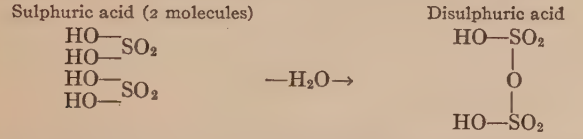
This process, known as the "contact method," is now displacing the leaden chamber method. It requires care, but the conditions of success are known and it is in extended use. It is a catalytic method.

Pure sulphuric acid is a colorless, oily liquid, of a specific gravity of 1.848, boiling at about 640° F. (338° C.). It is highly corrosive and poisonous. Exposed to the air, it absorbs water in considerable amount. When added to water it produces heat, and the dilution of any considerable quantity must be performed by slowly pouring the acid into the water with constant stirring. Sulphuric acid will decompose many organic substances, extracting the hydrogen and oxygen in the proportion to form water, and leaving the carbon. This action may be termed "dehydrolysis," as it is the reverse of that action of water termed "hydrolysis" (see p. 45). The commercial acid is usually more or less brown, or even black, from the carbon set free from particles of dust, straw, etc., which accidentally fall into it. It always contains a small quantity of water—about one molecule to twelve of acid:—

$$H_2O + 12H_2SO_4.$$

The boiling point, and many other properties, are practically the same as those of the pure acids.

Nordhausen or Fuming Sulphuric Acid, the original *oil of vitriol*, is obtained by the distillation of green vitriol. It corresponds to the formula $H_2S_2O_7$, being two molecules of sulphuric acid minus one of water, $2H_2SO_4 - H_2O = H_2S_2O_7$. Acids derived in this way are known as di-acids or pyro-acids. The graphic formula is—



It is denser and even more corrosive than the common acid, and unites with water with great energy. It is used for dissolving indigo and for a few other purposes. When heated, sulphur trioxide distils off, and the ordinary acid is left.

The properties of sulphuric acid are greatly modified by dilution; its corrosive and charring action may be entirely removed by adding much water.

The salts of sulphuric acid are called sulphates. Monads give two sulphates, acid and normal. Sodium gives—

Acid sodium sulphate	Sodium sulphate
$NaHSO_4$	Na_2SO_4

Dyads give one sulphate. Barium yields only $BaSO_4$, barium sulphate.

Commercial sulphuric acid contains several impurities, of which the most important are arsenic and lead.

Thiosulphuric acid, $H_2S_2O_3$, is commonly but erroneously called hyposulphurous acid. Sodium thiosulphate is much used in photography; it is the "hypo" of the photographer. These compounds may be regarded as sulphuric acid in which one atom of oxygen is replaced by sulphur; hence thiosulphuric, not thiosulphurous, acid. The formula may be written thus: $HS - SO_2 - OH$. The thiosulphates are powerful reducing agents.

Sulphur forms several compounds with chlorine: S_2Cl_2, sulphur chloride; SCl_2, sulphur dichloride; SCl_4, sulphur tetrachloride.

Selenium, Se, 79.2, is found native and also as selenide. It is rare.

The physical properties of selenium resemble those of sulphur. It has the property of changing its electric conductivity under the influence of

light. It is not alone in this respect but is most active. Some applications of the property have already been made.

The compounds of selenium are analogous to those of sulphur:

H_2Se	Hydrogen selenide.
SeO_2	Selenium dioxide.
H_2SeO_3	Selenous acid.
H_2SeO_4	Selenic acid.

Tellurium, Te, 127.5, is found native, and also in union with bismuth, gold, etc. It is rare.

It has a pinkish metallic luster, fuses just below a red heat, and boils at a somewhat higher temperature.

PHOSPHORUS

Phosphorus, P, 31, occurs principally as calcium phosphate, which exists in bones and teeth, and in many minerals. Phosphates also exist in the fluids of the animal body. It is often prepared from bones, which contain from one-third to two-thirds their weight of calcium phosphate. The bones are burned, and from the *bone ash* the phosphorus is obtained.

Phosphorus when freshly prepared is a light yellow, soft solid; when kept for some time, especially in the light, it becomes brownish, opaque and harder. It is kept under water. It takes fire easily, and burns with a bright flame, producing white clouds of phosphoric anhydride, P_2O_5. Exposed to air at low temperature, it can still undergo a slow combustion, producing P_2O_3; it is then luminous in the dark. It is insoluble in water, but dissolves in oils and in carbon disulphide. It is very poisonous. It melts at 111° F. (43° C.), and boils at 550° F. (288° C.). By keeping it at a temperature of 450° F. (232° C.) for some hours, in a closed vessel, it is converted into the *amorphous* or *red phosphorus*, an allotropic form, which is red, insoluble in carbon disulphide, difficult to burn, non-poisonous, and shows many other minor differences. Its composition is the same.

Phosphorus is used in matches and in a mixture, "phosphorus paste," used for killing vermin.

In all experiments with phosphorus great care must be taken, as it is easily inflamed and produces severe burns. It should be handled with a pair of forceps, and cut under water.

Phosphorus acts as a triad or pentad; its affinities in the free state are very high. It is a powerful reducing agent. In minute quantity it may be detected by its luminosity when distilled in a dark room.

Hydrogen Phosphide, PH_2, *Phosphine*.—This body is formed under conditions analogous to those which produce ammonia. When a solution of sodium hydroxide is boiled with phosphorus, hydrogen phosphide is formed.

The reaction is—

$$3NaHO + 3H_2O + P_4 \rightarrow 3NaH_2PO_2 + PH_3.$$

NaH_2PO_2 is sodium hypophosphite. Hydrogen phosphide is a colorless gas of a disagreeable odor. As ordinarily made it is spontaneously inflammable, but this is due to the presence of a small quantity of the vapor of a liquid phosphide, PH_2, *phosphidogen*. If this latter is removed by passing the fresh gas through a tube placed in a freezing apparatus, the power of inflaming spontaneously is lost.

Hydrogen phosphide forms many compounds analogous to those formed by ammonia.

Compounds of Phosphorus with Oxygen.—Only two compounds are definitely known. These are:—

P_2O_3..... Phosphorous anhydride or phosphorous oxide.
P_2O_5..... Phosphoric anhydride or phosphoric oxide.

Phosphorous Anhydride, P_2O_3, is produced by the slow oxidation of phosphorus.

Phosphoric Anhydride, P_2O_5.—This is easily produced by burning phosphorus in the air. It is a snow-like solid, which rapidly absorbs water. It is capable of uniting with water in at least three proportions, forming different bodies. The combination is shown in the following equations:—

$P_2O_5 + H_2O \rightarrow 2HPO_3$..... Metaphosphoric acid.
$P_2O_5 + 2H_2O \rightarrow H_4P_2O_7$..... Pyrophosphoric "
$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$..... Orthophosphoric "

The third acid yields the common phosphates.

Metaphosphoric acid is distinguished by its power of coagulating albumin. Although the three phosphoric acids differ in oxygen, the termination "ic" is not changed, because they are all formed from the same anhydride, and all contain pentad phosphorus. The difference in oxygen is due to the water introduced in forming the acid. The number of salts formed by each acid is in proportion to the number of molecules of water involved in its formation:

Metaphosphoric acid, produced by adding *one* molecule of water, gives *one* series of salts:—

$NaPO_3$..... Sodium metaphosphate.
$Ca(PO_3)_2$..... Calcium "

Pyrophosphoric acid, produced by adding *two* molecules of water, gives *two* series of salts, acid and normal:—

$Na_2H_2P_2O_7$..... Acid sodium pyrophosphate.
$Na_4P_2O_7$..... Sodium "

Orthophosphoric acid, produced by adding *three* molecules of water, gives *three* series of salts, di-acids, acid and normal:—

NaH_2PO_4..... Di-acid sodium orthophosphate.
Na_2HPO_4..... Acid " "
Na_3PO_4..... Sodium orthophosphate.

Sodium, potassium and ammonium phosphates are mostly soluble in water. Almost all others are insoluble in water, but soluble in acids.

A solution of ammonium molybdate in nitric acid gives with orthophosphates a bright yellow precipitate. This is a very delicate test.

Two phosphorus chlorides are known, PCl_3 and PCl_5.

ARSENIC

Arsenic, As, 75, occurs in the free state and as sulphide, also in combination, with nickel, cobalt and iron. It is rather abundant, and exists in small amounts in many minerals. It must not be confused with the common poison, arsenous oxide, As_2O_3, also called "arsenic."

It is prepared by deoxidizing arsenous oxide by charcoal:—

$$As_2O_3 + C_3 \rightarrow As_2 + 3CO.$$

When freshly prepared it is a steel-gray, brittle mass with a decided luster. It tarnishes somewhat in the air, and passes into vapor at about 356° F. (180° C.) without fusing. Heated in contact with air, it oxidizes to arsenous oxide, and develops a garlicky odor. It is not dissolved by any simple solvent.

Arsine, AsH_3, *Hydrogen Arsenide.*—This body is analogous to ammonia; its formation is a delicate test for arsenic. The usual method of preparation is to liberate hydrogen in a solution of arsenous oxide. It is a combustible gas of disagreeable odor and very poisonous.

Compounds of Arsenic with Oxygen:—

As_2O_3..... Arsenous oxide or arsenous anhydride.
As_2O_5..... Arsenic " " "

Arsenous Oxide, White Arsenic, Arsenous Anhydride, As_2O_3.—This is the substance usually called "*arsenic.*" It presents itself in commerce in two varieties: (*a*) The vitreous form, transparent and colorless at first, but afterward becoming yellowish and porcelain like; (*b*) a pulverulent form, which is distinctly crystalline.

Arsenous oxide is a white solid, odorless and tasteless, dissolving with difficulty and only in small amounts in cold water; the solution is feebly acid, and is supposed to contain arsenous acid, H_3AsO_3. Hot water is a more active solvent. A fluidounce of cold water will dissolve about 1 grain, and the same amount of water if kept for one hour at the boiling point will take up at least 12 grains. In acid and alkaline solutions it dissolves much more readily. Heated to 380° F. (190° C.), the solid passes into vapor without fusing, and if allowed to condense produces brilliant, transparent crystals. It is intensely poisonous in all its forms, a few grains being a dangerous dose. It is used in medicine, also in the manufacture of colors, and for many other purposes. Its frequent occurrence and poisonous qualities have made its properties and tests of great importance. The following is a brief summary of the methods used:—

1. *Reduction Test.*—A small quantity of powdered arsenous oxide is mixed with some dried potassium ferrocyanide and heated in a narrow glass tube. Arsenic (element) is set free, rises in vapor, and condenses on a cooler portion of the tube, as a dark steel-gray but rather lustrous layer, called the *arsenical mirror.* If this deposit is heated, it may be driven further along the tube, and will finally oxidize and produce crystalline arsenous oxide.

2. *Sublimation Test.*—Arsenous oxide heated alone passes quickly into vapor, and by allowing this vapor to condense upon a *slightly warmed* part of the tube fine crystals are formed. The crystals are octahedral, but are rarely completely formed. Very minute quantities of arsenic can be recognized by this test with the aid of the microscope.

3. *Reinsch's Test.*—This is the most valuable test, because it can be applied to impure mixtures, such as the contents of a stomach. A small quantity of water is put into a wide test-tube or porcelain basin; some hydrochloric acid is added; a piece of clean copper is put in and the water brought to boiling. A few drops of the suspected solution are now added, and if an arsenic compound is present a dull, steel-colore ddeposit of copper arsenid will soon form on the copper. When this deposit has become rather dense, the copper is taken out, dried with filter paper,

rolled up into small bulk, and placed in the end of a small glass tube. Heat being applied, the deposit is oxidized and volatilized, forming octahedral crystals of arsenous oxide.

4. *Marsh's Test.*—This depends on the power of nascent hydrogen to form arsine, AsH_3. The hydrogen is obtained either by the action of sulphuric acid upon zinc or magnesium, of sodium amalgam on water, or by a current of electricity. Arsine is combustible. If a cold porcelain plate be held in the flame, a soot of arsenic will be deposited as a brown, shining stain. If the tube which is conducting the current be heated, the gas will be decomposed and a similar stain formed within the tube. The stains may be identified by the fact that they are: (*a*) Easily volatile; (*b*) soluble in a solution of bleaching powder; (*c*) capable of producing octahedral crystals of arsenous oxide.

Three tests, known as the liquid tests, are applicable only to pure solutions of arsenous compounds. They are—

1. Hydrogen sulphide produces a lemon-yellow precipitate of arsenous sulphide, As_2S_3:—

$$As_2O_3 + 3H_2S \rightarrow As_2S_3 + 3H_2O.$$

The solution must be slightly acid. A few drops of hydrochloric acid will suffice.

2. Silver nitrate made feebly alkaline by ammonium hydroxide gives a yellow precipitate of silver arsenite.

3. Copper sulphate, made feebly alkaline, gives a green precipitate of copper arsenite.

Arsenic Oxide, As_2O_5.—This is produced by oxidizing arsenous oxide with nitric acid. It forms with water arsenic acid, H_3AsO_4, which has been used as an oxidizing agent in the manufacture of coal-tar colors. This use has been supposed to account for the case of skin irritation which have been occasionally observed to follow the wearing of goods dyed with these colors, but it is doubtful if any of the poison remains in the manufactured fabric.

Arsenic acid forms salts called arsenates. Three forms of arsenic acid are known, corresponding to the three forms of phosphoric acid.

Compounds of Arsenic and Sulphur.—Three of these are known:—

AsS.....Arsenic monosulphide, *realgar.*
As_2S_3.....Arsenous sulphide, *orpiment.*
As_2S_5.....Arsenic "

Realgar is a brick-red solid, easily volatile. It may be considered as analogous to NO. It is often written as As_2S_2.

Orpiment, King's yellow, is found as a mineral and is easily produced artificially by the action of hydrogen sulphide upon arsenous compounds. It is a bright yellow solid, fusible and volatile, soluble in alkalies, but insoluble in water and dilute acids. It is often obtained in the process of testing for arsenic, and is used as a pigment.

Arsenic forms chlorides, bromides and iodides, but they are not important.

BORON

Boron, B, 10.8, is found in the form of boric acid, H_3BO_3, in steam jets in volcanic regions, and also as deposits of sodium borate or calcium borate. It has been obtained as a dark green powder, and in a crystalline form, resembling the diamond in hardness. Boron is a triad, and bears some resemblance in chemical functions to carbon and aluminum.

Boric Acid, H_3BO_3, *Boracic Acid.*—This exists in the steam discharged in some volcanic regions; some of its salts occur as minerals. It forms bitter pearly scales, soluble in water and alcohol (the solution in water is only slightly ionized, hence is but feebly acid). Heated to 248° F. (120° C.), it forms metaboric acid, HBO_2, and by further heating is converted into borci anhydrid, B_2O_3, which fuses to a clear glass. Its salts are called borates. Boric acid is an antiseptic. Several preparations of boric acid or of borates are now in the market as food preservatives. A compound prepared by the incorporation of boric acid with glycerol, is also employed as a preservative.

Boric acid ionizes but slightly and therefore shows but feeble acid properties. It turns turmeric paper brown-red. It imparts a bright green color to flame.

Borax, $Na_2B_4O_7$, sometimes called *sodium biborate,* is the most familiar compound of boron, and may be regarded as sodium tetraborate. Tetraboric acid is not known in the free state, but can be theoretically derived by subtracting one molecule of water from four molecules of metaboric acid:—

$$4HBO_2 - H_2O \rightarrow H_2B_4O_7.$$

Borax has the power to take up oxides and re-form metaborates, and, as the compounds are fusible at moderate heat, borax is frequently used in metallurgical operations (*e. g.*, soldering) to clean off the surfaces of metals, which it does by dissolving the oxides.

CARBON

Carbon, C, 12, occurs very abundantly in nature. It is so constant a component of organic bodies that organic chemistry has been called the chemistry of the carbon compounds. In the tissues of animals and plants it exists in union with hydrogen, oxygen and nitrogen. The various forms of coal and graphite, and some carbonates, especially calcium and magnesium carbonates, are abundant minerals. Carbon is seen in several forms.

Amorphous Carbon, such as lampblack and charcoal.

Graphite, Plumbago (*black lead*), a crystalline form.

Diamond, crystalline, often chemically pure.

These forms are insoluble in all ordinary liquids, infusible and unacted upon by acids and alkalies or by the air at ordinary temperatures. Heated strongly in air or oxygen, they burn, producing CO or CO_2.

Lampblack is the deposit from smoky flames. It generally contains hydrogen. *Wood charcoal* contains some hydrogen and the mineral substances of the wood.

Animal charcoal is obtained by charring animal tissues and generally contains considerable calcium phosphate and some calcium carbonate.

Wood and animal charcoals have great powers of absorption—the former for gases, the latter for organic matters, especially colors and bitter principles.

This property of wood charcoal explains its use as a deodorizer. Gases containing hydrogen, sulphur or phosphorus are generally entirely decomposed when absorbed by charcoal. During the world war, extensive use was made of the power of charcoal to absorb gases, in the construction of gasmasks. Researches in American laboratories resulted in the discovery of methods for producing charcoals from ordinary coal as well as from wood, and products of high absorbent activity are now available.

If a solution of some organic color, such as litmus or cochineal, be filtered through animal charcoal, the color will be partly or wholly removed. Bitter principles, will also be removed. Animal charcoal is extensively used for the decolorization of syrups and vegetable infusions.

Graphite (*plumbago, black lead*) is destitute of absorbent properties, and is used for lead pencils and for crucibles.

Diamond is a crystalline form of carbon. It is the hardest substance known, and has been used with great advantage for the drilling and cutting of hard materials.

The specific gravity, color and hardness differ in the different forms of carbon, but they are not true allotropic modifications.

Coal has been formed from organic matter. Bituminous or soft coals contain much hydrogen and some oxygen. Coke is the residue after heating soft coal. Anthracite has very little hydrogen. It yields no gas on heating.

Carbon is usually a tetrad, and combines with many elements.

Compounds of Carbon with Hydrogen.—Hydrogen and carbon combine in many proportions.

Illuminating Gas.—When bituminous coal is heated in a closed vessel, a large amount of gas is given off. This gas, after being purified, constitutes illuminating gas—consisting largely of hydrogen, methane, CH_4, and ethene, C_2H_4. This is the original *coal gas*, but illuminating gas is now often *water gas* (see under "Carbon Monoxide").

Compounds of Carbon with Oxygen.—The important ones are—

Carbon monoxide	CO.
Carbon dioxide Carbonic anhydride	CO_2.

Carbon Monoxide, Carbonic Oxide, CO.—This is produced when carbon is burned in a deficient supply of air, as in stoves with defective draft and in the large furnaces for reducing and working iron, in which an excess of fuel is purposely maintained. When steam is thrown upon hot coal a mixture of carbon monoxide and hydrogen, generally called *water gas*, is produced. This is available as a gaseous fuel, or may be impregnated with hydrocarbons and used as a source of light.

For experimental purposes the action of sulphuric acid upon oxalic acid or upon potassium ferrocyanide is used for the preparation of CO.

One reaction is an example of "dehydrolysis," that is, the removal of H_2O from substances that contain hydrogen and oxygen in some other relation. Pure oxalic acid does not contain water, but when heated with sulphuric acid, it yields water by the following reaction:—

$$H_2C_2O_4 + H_2SO_4 \rightarrow H_2O + H_2SO_4 + CO_2 + CO.$$

The carbon dioxide may be absorbed by passing the gases through sodium hydroxide solution, when the carbon monoxide is obtained pure.

The reaction with potassium ferrocyanide is much more complex. It is an illustration of a chemical action which is observed with many substances containing nitrogen when heated with strong sulphuric

acid, the nitrogen is converted into ammonium sulphate (see under "Ammonium")—

$$K_4C_6N_6Fe + 6H_2SO_4 + 6H_2O \rightarrow 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO.$$

Carbon monoxide is a colorless, odorless, tasteless gas, of decidedly narcotic poisonous properties. It is a little lighter than air. It burns easily with a clear blue flame. It is an unsaturated molecule, and will combine with chlorine and some other elements. By reason of its unsaturated condition, it has the power to unite firmly with hemoglobin and prevent the proper oxidation of the blood, thus producing, when inhaled, a persistent asphyxiated condition. Poisoning by carbon monoxide has now become of common occurrence in consequence of the extended use of water gas and gasoline motor fuels. It is not unlikely that the unnoticed escape of this gas in houses is the cause of much discomfort and ill health.

Carbon Dioxide, Carbonic Anhydride, CO_2, often wrongly called carbonic acid, is an abundant substance occurring in air and water. Some of its compounds, especially calcium and magnesium carbonates, are common minerals. Carbon dioxide is produced in a great variety of ways:—

1. By the respiration of animals.
2. By ordinary combustion.
3. By fermentation and decay.
4. By decomposition of carbonates, either by heat or by acids.

The reaction in the case of chalk and hydrochloric acid is—

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2.$$

It is unimportant whether the water and CO_2 be considered as separate or united to form carbonic acid, H_2CO_3. By passing the escaping gas over dry calcium chloride or strong sulphuric acid, the pure CO_2 may be collected.

Properties.—Carbon dioxide is a colorless gas of a somewhat sharp taste. It is soluble at ordinary pressure in its own bulk of water, and the solubility is increased in proportion to the pressure. It is about 50% heavier than air. 1 liter weighs 2.07 grams. It can be liquefied by pressure and cold. The liquid freezes at $-70°$ F. ($-56°$ C.). It does not support animal life nor ordinary combustion; but bodies of high affinity, if already in active combustion, will decompose it and continue to burn. Red-hot coal will produce the following reaction: $C + CO_2 \rightarrow 2CO$, which accounts for the production of carbon monoxide in ordinary stoves. A

lighted taper put into the gas is instantly extinguished, but ignited magnesium will continue to burn and deposit carbon. The reaction is $Mg_2 + CO_2 \rightarrow 2MgO + C$.

Lime water is instantly rendered turbid by the gas, from the formation of insoluble calcium carbonate, thus constituting a test for the gas.

Carbon dioxide has a tendency to accumulate at low levels if produced in large amounts. It is found in undue proportions at the bottom of mine shafts and in fermenting vats. Instances of suffocation often occur in these places. The usual method of determining whether such places are safe to enter is by lowering a lighted candle; if this continues to burn vigorously, the air is probably safe; if it burns feebly or is extinguished, the air contains too much of the gas.

Aided by the action of frost, carbon dioxide breaks down and renders soluble many kinds of rocks and converts them into soils. The ordinary effervescing soda water is an artificial solution of the gas under pressure. Fermenting liquids owe their effervescence to the same cause. Under the influence of light, plants decompose it, the carbon being absorbed and the oxygen given off.

Carbonic acid forms a series of salts called the carbonates. Monads form two salts. Potassium gives—

$KHCO_3$..... Acid potassium carbonate.
K_2CO_3..... Potassium carbonate.

Dyads give one salt—

$CaCO_3$..... Calcium carbonate.

Carbonic acid is easily recognized by its rendering turbid a solution of calcium hydroxide (lime water) or barium hydroxide (baryta water). It turns litmus to a wine red, the blue color being restored on boiling.

Most carbonates are only slightly soluble in water and may, therefore (see p. 18), be obtained by precipitation of a soluble carbonate by a solution of a salt of the element the carbonate of which is desired. Thus, calcium carbonate can be obtained by mixing solutions of calcium chloride and sodium carbonate—

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl.$$

In many cases, however, a partial hydrolysis (see p. 45) occurs, and some hydroxide is formed. Thus, a mixture of magnesium sulphate and sodium carbonate shows both the following reactions, the first representing the most abundant products:—

$$MgSO_4 + Na_2CO_3 \rightarrow Na_2SO_4 + MgCO_3,$$
$$MgSO_4 + Na_2CO_3 + H_2O \rightarrow Na_2SO_4 + MgH_2O_2 + CO_2.$$

With some elements the action is almost, or wholly, controlled by the hydrolysis, little or no carbonate being formed. This occurs with aluminum salts, as illustrated by the reaction—

$$Al_2(SO_4)_3 + 3Na_2CO_3 + 3H_2O_3 \rightarrow 3Na_2SO_4 + Al_2H_6O_6 + 3CO_2.$$

Carbon Oxychloride.—$COCl_2$, phosgene. This is a very poisonous gas which was largely used as an asphyxiating agent during the world war.

Combustion and the Structure of Flame.—Carbon, hydrogen, oxygen and nitrogen are the usual elements of the tissues of animals and plants from which fuel and illuminating agents are mostly derived. Burning is usually the absorption of oxygen and formation of carbon dioxide, water and free nitrogen, and sometimes small amounts of ammonia and nitric acid. Ordinary flame is gas of some kind in the process of uniting with the oxygen of the air.

Formerly the terms "combustible" and "supporter of combustion" were much used; carbon, phosphorus and hydrogen being examples of combustible elements; oxygen and chlorine, supporters of combustion. This distinction is now abandoned; the action is a mutual one, and the supporter of combustion may easily be made the combustible.

Common flames consist of three parts: (*a*) An inner blue space, (*b*) a shell of luminous particles, (*c*) a fringe of feebly luminous particles.

The inner part is the point at which the gas that is burning is produced or escapes. This consists, in most cases, principally of carbon and hydrogen, which are largely oxidized. Complete combustion occurs in the outer portion, producing the feeble fringe of light, which is the third part. Substances deficient in carbon, or burned in a supply of oxygen sufficient to consume the carbon quickly, produce little light; on the other hand, if the quantity of carbon is large, the flame will not be able to heat it above a red heat, and the supply of oxygen may not be sufficient to burn all of it, producing a red, smoky flame.

Alcohol, which contains little carbon, burns without much light; turpentine, which contains much carbon, burns with a red flame and smoke. With a mixture of the two a good flame may be obtained.

The exact physical condition and chemistry of ordinary luminous flames are not clearly established. The old view was that the luminous zone consists of the hydrogen undergoing combustion and by that means heating the carbon, set free in very fine division, to a white heat. This carbon

was thought to proceed to the outer zone and burn to carbon dioxide. This view is not now accepted, and no satisfactory substitute has been offered.

Anything which cools a flame may cause it to deposit carbon; hence the formation of soot or lampblack when flames come in contact with cold surfaces.

If a chimney is placed over a smoky flame, the increased draft causes a more abundant supply of air, and the carbon is completely burned. This is the reason for the use of chimneys with oil lamps.

If a flame is suddenly cooled, as by the introduction of a coil of wire or a sheet of wire gauze, the combustion will cease and the mixture of gas and air will escape. This can be easily shown by putting a piece of wire gauze across a gas flame, when it will be found that the flame will stop at the gauze, but a combustible mixture of gas and air will pass through it. Similarly, the gas may be lighted above the gauze and the flame will not run back. If the gauze becomes hot, the flame will pass through. This principle is made use of in Davy's safety lamp for preventing explosions in mines. It consists of a lamp arranged so that no air or gas can get in except through fine gauze. If an explosive mixture finds its way to the flame, its combustion is limited to the interior of the lamp, at least for a time.

Illuminating gas, mixed with air, will burn with a non-luminous, smokeless flame. Lamps for such use are now common. In the simplest form, the Bunsen burner, the air is drawn in through openings at the bottom. Many forms of these lamps are now made.

When a current of air is driven into a flame its temperature is increased. This is the cause of the efficiency of the mouth blowpipe and of blast lamps.

When mixtures of gas and air are ignited, combustion may occur through the entire mass at once. This constitutes an explosion. Violent explosions may occur from the rapid ignition of fine particles of coal, flour, or other combustible material diffused through the air.

Flame Tests.—Many elements give characteristic colors to flames. Such tests are very delicate, and when applied to pure substances very satisfactory. When several elements are present, one color may conceal the other, and thus the test be worthless. By passing the light through a prism, the colors are separated, and each may be recognized. The apparatus for this purpose is called a spectroscope. Observations with it show that most elements give out light which is made up of several colors.

Carbon Disulphide, CS_2.—This is analogous to carbon dioxide. It is obtained by direct combination of its elements. It is a colorless liquid, which, when quite pure and in large quantity, has a rather pleasant odor, but when impure, and especially when diffused through the air in small quantity, is quite disagreeable. It is very volatile and inflammable, and has high solvent powers, dissolving sulphur, phosphorus and most oils and fats, and is much used for such purposes. Its vapor will take fire much below a red heat.

Carbon Chloride.—Carbon forms several compounds with chlorine:—

Marsh gas, CH_4, for instance, yields, by successive substitution action, the following compounds:—

CH_3Cl_3	Monochlormethane.
CH_2Cl_2	Dichlormethane.
$CHCl_3$	Trichlormethane.
CCl_4	Tetrachlormethane.

The third body, $CHCl_3$, is chloroform; the fourth is carbon tetrachloride.

Cyanogen, CN.—Cyanogen is a radical, and in its chemical relations resembles such elements as Cl, Br and I. It forms compounds called *cyanides*. In all of these it acts as a monad: for instance, hydrogen cyanide, HCN, potassium cyanide, KCN. Dyads require two molecules of cyanogen. Calcium cyanide is CaC_2N_2 or $Ca(CN)_2$. The abbreviation Cy is sometimes used instead of the symbol CN. HCy is written instead of HCN, KCy instead of KCN.

SILICON

Silcion, Si, 28, occurs very abundantly as oxide, SiO_2, and as silicates. Silicon exists in several forms, somewhat analogous to those of carbon. When strongly heated in the air it burns, producing SiO_2.

Silicon is tetrad, and is related to carbon in many ways. Compounds have been obtained in which it replaces carbon.

Silicon Dioxide, Silica, Silicic Anhydride, SiO_2.—This is a widely distributed substance, occurring as common sand, chalcedony, flint, and forming silicates of which clay, granite, feldspar and sandstones are instances. A very large proportion of the solid substances in the earth's crust is in the form of compounds of silicon. Silicon exists in the stems of grasses and in the teeth and bones of animals.

In its pure forms silicon dioxide is a colorless, nearly infusible and insoluble solid, destitute of chemical activity. In nature it often occurs

in large six-sided crystals, called quartz or, when ruby colored, amethyst. It also occurs in various amorphous conditions—agate, jasper, chalcedony and onyx. In all its forms it is converted into a silicate by fusion with sodium carbonate. When lime, lead oxide or other metallic oxides are mixed with the sodium silicates, glass is produced. When a large excess of sodium carbonate is used, the glass is soluble in water, and is commonly known as *soluble glass* or *liquid silex*. It is used as a cement and in soaps.

Silicic Acid.—Several silicic acids are known. If sodium silicate be treated with hydrochloric acid, the following reaction occurs:—

$$Na_4SiO_4 + 4HCl \rightarrow 4NaCl + H_4SiO_4.$$

This is called orthosilicic acid. Part of it remains in solution. It is tasteless and feebly acid to litmus. By evaporation it forms a gelatinous mass which can be brought to the composition H_2SiO_3 (metasilicic acid), and by further heating gives the insoluble anhydride.

Silicon combines with the halogens, forming bodies resembling the corresponding carbon compounds.

Silicon and fluorine have a strong affinity, forming silicon fluoride, SiF_4. Silicon combines with positive elements, forming silicides, but many of these are of uncertain composition. Hydrogen silicide, H_4Si, produced by the action of acids upon magnesium silicide, takes fire spontaneously. In its composition it is analogous to marsh gas, H_4C. Many hydrogen silicides have been obtained analogous to hydrocarbons, but they have as yet only theoretic interest.

POTASSIUM

Potassium, K, 39.1, occurs in many rocks and soils and in the ashes of land plants, also as nitrate and chloride. It is quite soft, quickly tarnishes in the air, and decomposes water rapidly, the escaping hydrogen being so highly heated as to take fire, burning with a purple flame, due to the potassium. Sp. gr., 0.865. It is highly positive, and forms several oxides.

Potassium Hydroxide, KHO, *Caustic Potassa,* is made by boiling potassium carbonate with slaked lime:—

$$CaH_2O_2 + K_2CO_3 \rightarrow 2KHO + CaCO_3.$$

It is a white solid, freely soluble in water, forming a strongly alkaline liquid.

Potassium Carbonate, K_2CO_3, *Salt of Tartar.*—This is extracted from the ashes of land plants. Pure potassium carbonate is white, alkaline and moderately corrosive.

Acid Potassium Carbonate, $KHCO_3$, *Salæratus*, is a white crystalline body, and is used in effervescing mixtures, but acid sodium carbonate has of late years substituted it to a great extent. It is often called *bicarbonate*.

Potassium Sulphate, K_2SO_4, forms hard crystals, not very soluble in cold water.

Acid Potassium Sulphite, $KHSO_4$, is sour and strongly acid to test paper. It is often called bisulphate.

Potassium Nitrate, KNO_3, *Niter*, *Saltpeter*, is found on the surface of the soil in India, and may be prepared artificially. Potassium nitrate is used in gunpowder and fireworks.

Gunpowder consists of niter, charcoal and sulphur. The gases produced at the moment of combustion occupy about 1200 times the bulk of the power; the bursting effect is due to this sudden expansion.

Potassium Chlorate, $KClO_3$.—The salt forms flat, tabular crystals. It melts below a red heat, and at a little higher temperature gives off all its oxygen, leaving potassium chloride. It is not very soluble in cold water, requiring about sixteen times its weight for solution. It is used largely as a source of oxygen.

Potassium Chloride, KCl, exists in sea water and in some springs. It resembles common salt.

Potassium Bromide, KBr, forms cubical crystals, soluble in water.

Potassium Iodide, KI, closely resembles the bromide. It is easily soluble in water.

Potassium compounds are mostly soluble in water. A few, however, are so slightly soluble as to afford us serviceable tests.

Platinum chloride produces, with potassium salts, a yellow crystalline precipitate of potassium chloroplatinate, K_2PtCl_6.

Tartaric acid gives a white crystalline precipitate of acid potassium tartrate, $KHC_4H_4O_6$.

Potassium compounds give to flame a color which is a mixture of red and violet.

SODIUM

Sodium, Na, 23.—Common salt, NaCl, is the most abundant compound. The ashes of sea plants contain sodium carbonate. Sodium closely resembles potassium, but is a little heavier and not so easily oxidized. Its compounds are also much like those of potassium.

Sodium Dioxide, Sodium Peroxide, Na_2O_2, is now a commercial article and is a very useful oxidizing agent. It is a yellowish solid, very caustic. It dissolves readily in water, evolving some oxygen.

Sodium Hydroxide, NaHO, *Caustic Soda,* is very strongly alkaline and corrosive. It is prepared from sodium carbonate, in the same manner as potassium hydroxide. It is a powerful poison.

Sodium Carbonate, Na_2CO_3, forms large crystals, having the composition Na_2CO_3, $10H_2O$, called *sal soda* or *washing soda.* On exposure to air these crystals effloresce, and fall to a white powder. A monohydrated sodium carbonate, Na_2CO_3,H_2O, is now a commercial article. Crude sodium carbonate is called *soda ash.*

Acid Sodium Carbonate, $NaHCO_3$, *Baking Soda,* commonly called *bicarbonate,* is now much used in effervescing mixtures, such as the common baking powders, which are usually a mixture of cream of tartar and baking soda. Alum and acid calcium phosphate are often used as substitutes for the cream of tartar. The action of the powder is due to the sudden evolution of a large volume of carbon dioxide:—

$$NaHCO_3 + KHC_4H_4O_6 \rightarrow NaKC_4H_4O_6 + H_2O + CO_2.$$

Sodium Sulphate, Glauber's Salt, Na_2SO_4, $10H_2O$, forms large crystals, which are more soluble in water at 93° F. (34° C.) than at any other temperature.

Sodium Nitrate, $NaNO_3$, *Chili Saltpeter,* is used as a fertilizer, and also in the preparation of nitric acid.

Sodium Chloride, NaCl, *Common Salt,* occurs in thick beds in various parts of the world, and is also prepared from sea water and certain brine springs, by evaporation. It dissolves in about the same amount in hot and cold water.

Sodium Fluoride, NaF, is used as a food preservative, and as a vermin killer. It is usually sold as a white powder.

Sodium Phosphates.—The most important form is disodium acid phosphate, Na_2HPO_4, which is used in medicine. Sodium phosphate, Na_3PO_4, is now made in large quantity as a cleansing agent and for other purposes.

Sodium Tetraborate, $Na_2B_4O_7$. See Boric Acid.

Sodium Silicate. See Silicon.

Sodium Thiosulphate, $Na_2S_2O_3$, is much used in photography under the name *hyposulphite.* Its solution possesses the power of dissolving many of the salts of silver, which are insoluble in water.

Sodium Sulphite, Na_2SO_3, is used as a substitute for sulphurous acid in preventing fermentation, also as a reducing agent.

Sodium compounds give a strong yellow color to flame, and are with very few exceptions freely soluble in water. Uranium sodium magnesium acetate is almost insoluble in water.

LITHIUM

Lithium, Li, 7.—Its principal sources are some rather rare minerals. Its salts resemble in the main those of potassium and sodium. Small amounts of lithium compounds are occasionally found in natural waters, constituting the so-called *lithia waters*. Lithium imparts a crimson color to flame.

Cesium, Cs, 132.8, and Rubidium, Rb, 85.5.—The compounds of these are rare and resemble those of potassium. Cesium gives a blue color to flame; rubidium a dark red color.

AMMONIUM

Although not an element, ammonium has such close relations to the elements of this group, in the properties and uses of its compounds, that it is most conveniently considered at this point.

Ammonium compounds are usually less active than the corresponding compounds of potassium and sodium. Thus, ammonium hydroxide is feebler and less corrosive than sodium hydroxide or potassium hydroxide.

Ammonium Hydroxide, NH_4HO, the result of the solution of ammonia in water, is a colorless liquid, corrosive, poisonous, powerfully alkaline and pungent. It is commonly called "*ammonia water*" or simply "*ammonia*."

Ammonium Carbonate $(NH_4)_2CO_3$, is not generally seen. The body sold as ammonium carbonate is a mixture of acid ammonium carbonate with ammonium amino-carbonate (see under amino-compounds), therefore, $NH_4HCO_2 + NH_4(NH_2CO_2)$. It is often called *sesquicarbonate, or smelling-salt.* It is a white body, soluble in water, and smelling strongly of ammonia. By exposure to air it is converted into acid carbonate, NH_4HCO_3.

Ammonium Nitrate, NH_4NO_3, is a white solid, very soluble in water. Its chief use is for making nitrous oxide.

Ammonium Sulphate $(NH_4)_2SO_4$, is used as a fertilizer and in the manufacture of alum. It is formed in many cases when organic bodies containing nitrogen are heated with strong sulphuric acid. This action is now extensively utilized in the analysis of organic substances, especially food articles and fertilizers. It is commonly known as the "Kjeldahl method" from name of the discoverer (see under "carbon monoxide").

Ammonium Chloride Sal Ammoniac, NH_4Cl, is a white solid, crystallizing in cubes, and is very soluble in water. It has many uses. It is often called *muriate of ammonia.*

Ammonium Bromide, NH_4Br, *Ammonium Iodide*, NH_4I, are used in photography and medicine.

If dry ammonium compounds are heated with lime, ammonia is quickly evolved, and may be recognized by its odor, alkaline reaction, and the white cloud of NH_4Cl produced by hydrochloric acid. The most delicate test for ammonium is *Nessler's reagent*, a solution made by mixing $HgCl_2$, KI, and KHO or NaHO. This produces, with very minute quantities of ammonium, a yellow color. One part in fifty million parts of water can be recognized.

Ammonium Fluoride, NaF, is a powerful antiseptic.

COPPER

Copper, Cu, 63.6, occurs native in large masses, also as sulphide (copper pyrites), oxide silicate and carbonate. In small amounts it is widely distributed in nature, occurring in many articles of food, and often in the human body, especially in the liver and brain. Copper is distinguished by its red color. It is heavy, specific gravity, 8.9; hard, and can be worked into thin plates or wire; melts at 1996° F. (1901° C.). It conducts heat and electricity very well, and resists the action of the air, but is slightly oxidized and dissolved by acids when in contact with air. Salt water and the acids of fruits will produce this effect, and hence the danger of using copper vessels for kitchen purposes. Copper furnishes some valuable alloys—brass, gun metal, bronze. It forms two sets of salts; in the *cupric* series, the metal is dyad and saturated; in the other, *cuprous*, the copper is unsaturated. The cuprous salts are mostly colorless and tend to absorb oxygen or other negatives, becoming saturated (cupric) compounds; the cupric salts are green or blue (see under "Copper Sulphate").

Copper Monoxide, CuO, *Cupric Oxide*, *Black Oxide*, is a heavy, black powder. Copper hydroxide, CuH_2O_2, formed when copper salts are mixed with sodium hydroxide, is a bluish green mass, dissolving in ammonium hydroxide, producing a clear, deep-blue liquid; but with sodium hydroxide no solution occurs except in the presence of some organic bodies, especially sugar, when a clear blue solution is also formed. If a solution containing sugar is boiled, the cupric hydroxide is changed to cuprous oxide, which is precipitated as a red or orange powder.

Copper Carbonate, $CuCO_3$, appears not to be known in the pure state. Various oxycarbonates, malachite and azurite exist as minerals, and similar compounds are obtained by the addition of carbonates to copper salts.

Copper Sulphate, $CuSO_4$, *Blue Vitriol*, *Blue Stone*, forms large blue crystals soluble in water, and having the composition $CuSO_4, 5H_2O$.

Copper sulphate is often used to prevent growth of algæ in reservoirs. It has been found that a small amount of it in solution will kill many forms of bacteria. Even pieces of metallic copper immersed in water will kill some bacteria in the course of a few hours. In this case, the copper in minute amount diffuses through the water in a form that is called "colloidal" copper.

Copper Chloride, $CuCl_2$, is in green crystals, soluble in water.

Copper Arsenite, $CuHAsO_3$, *Scheele's or Paris Green*, is a bright green powder. It is used for killing insects and also as a color. It is a violent poison. A compound containing copper acetate and arsenite is known as Schweinfurth green.

Cuprous Salts.—Cuprous Oxide, Cu_2O, is the result of the reducing action of sugar on a mixture of sodium hydroxide and cupric hydroxide. *Cuprous Chloride*, CuCl, is a white solid, insoluble in water. The cuprous salts are easily converted into cupric.

Copper gives a green tint to flame. Potassium ferrocyanide produces, in solutions containing copper, a mahogany brown precipitate of copper ferrocyanide. A clean piece of iron immersed in a solution of copper becomes quickly covered with a bright red coating of copper.

SILVER

Silver, Ag, 107.9.—Silver occurs native—that is, in the free state—in moderate abundance, also as sulphide, chloride and other compounds. It is nearly always present in small amounts in lead ores. It is white and highly lustrous, easily worked into plates and wire, and a good conductor of heat and electricity. Specific gravity, 10.5. It resists the action of oxygen and of caustic alkalies, but is attacked by sulphur and sulphides and by nitric acid. The sensitiveness of silver salts to light is the basis of photography. Silver melts at 1681° F. (916° C.). For use in the arts it is usually allowed with copper. The standard alloy of the English mint (sterling silver) contains $\frac{1}{12}$ copper; that of the United States mint (coin silver) $\frac{1}{10}$ copper.

Silver Oxide, Ag_2O.—Oxygen is absorbed by melted silver, but no combination is formed. When a solution of a silver salt is treated with potassium hydroxide, and the precipitate gently heated, silver oxide is formed.

Silver Nitrate, $AgNO_3$, is made by dissolving the metal in nitric acid. It forms colorless crystals, very soluble in water, and, when mixed with organic matter, blackened by light. It fuses at 426° F. (219° C.), and is often cast in sticks (*lunar caustic*) for use in surgery. The property of forming a black, difficulty soluble precipitate with organic matter is utilized in the manufacture of hair dyes and marking ink.

Silver Chloride, AgCl, is found as a mineral, and is easily formed artificially by adding any soluble chloride to silver nitrate:—

$$NaCl + AgNO_3 \rightarrow AgCl + NaNO_3.$$

It forms a heavy white precipitate like curdled milk, turning violet in the light, especially if organic matter is present.

Silver is easily reduced from most of its compounds by heat alone, and by reducing agents.

GOLD

Gold, Au, 197.2, occurs in the free state, often in veins in quartz, often in small grains in sand and gravel; sometimes alloyed with silver, copper or other bodies.

Pure gold is very heavy (specific gravity, 19.4), capable of being worked into thin plates or wire, and an excellent conductor of heat and electricity, The ordinary yellow appearance is due to much admixed white light. The true color, red, is obtained by repeated reflections. It melts at 1900° F. (1036° C.). Gold is unaffected by air, water, sulphur, or ordinary acids, even at high temperatures. Its compounds are reduced by heat, and by reducing agents in the cold. Chlorine or a mixture of nitric and hydrochloric acid (which contains free chlorine) dissolves it, forming a chloride. In the pure condition it is very soft and can be welded in the cold by pressure. Goldfoil is prepared in this form for dentists' use. For articles subjected to wear it is alloyed with copper or silver. The proportion of alloy is indicated by *carats*, pure gold being 24 carats, 18-carat gold being 18 parts gold and 6 parts alloy. Copper makes a red alloy; silver, a green alloy. The United States coin gold contains 90 % of gold alloyed with copper and silver. Two sets of compounds are known, aurous and auric, in which the metal is respectively a monad and a triad. The oxides are not bases; one appears to be an anhydride.

Au_2O	Aurous oxide.
Au_2O_3	Auric "
$AuCl$	Aurous chloride.
$AuCl_3$	Auric "

Auric Chloride is produced when gold is dissolved in nitro-muriatic acid. By adding to the liquid, free from excess of acid, some ferrous sulphate, the gold is thrown down as a brown powder.

CALCIUM

Calcium, Ca, 40, occurs mainly in the form of sulphate, carbonate, phosphate, and fluoride. It is light yellow and malleable; it oxidizes easily.

Calcium Oxide, Quicklime, CaO, obtained by heating the carbonate to redness ($CaCO_4 = CaO + CO_2$), is a white, infusible solid, which neutralizes the most powerful acids and combines with water with great energy, forming.

Calcium Hydroxide, Slaked Lime, CaH_2O_2, a soft, white, caustic powder, slightly soluble in cold water (about 75 grains to U. S. gallon). The solution is known as *lime-water;* a thick mixture of calcium hydroxide with water is known as *milk of lime.*

Calcium Carbonate, $CaCO_3$. In a non-crystalline condition this is seen as *chalk, marble* and *limestone;* in crystals it forms *Iceland spar* and *aragonite.* It is the chief constituent of shells. It may be prepared by adding sodium carbonate to calcium chloride:—

$$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl,$$

or by passing carbon dioxide through calcium hydroxide solution.

It is a white solid, almost insoluble in pure water. It dissolves more freely in water containing carbon dioxide, hence, many natural waters contain it. When present in an amount more than a few grains to the gallon, a *hard* water is formed, which has the property of curdling soap and preventing the formation of a lather, due to precipitation of insoluble calcium salts, formed from the soap. Boiling expels carbon dioxide, precipitates the calcium carbonate, and softens the water, hence, the hardness due to calcium carbonate is called *temporary* hardness. The excess of carbon dioxide will also be lost by exposure to air, and calcium carbonate will then be deposited. Such an action occurs in caves, forming *stalactites* and *stalagmites.*

Calcium Sulphate, $CaSO_4$, usually occurs crystallized with $2H_2O$, constituting *selenite, gypsum* and *alabaster,* sometimes, however, anhydrous. It is soluble in about 400 times its weight of cold water. It is a frequent ingredient of natural water, causing the same effect of hardness mentioned above; but as it does not owe its solubility to carbon dioxide, boiling does

not soften the water, and hence the condition is called *permanent* hardness. When the crystallized mineral is heated moderately, it loses some water and becomes a soft white powder, *plaster of Paris*, which when mixed again with water reabsorbs it and becomes a hard mass, expanding slightly in bulk, and thus suited for taking casts of any object.

Calcium Phosphate, $Ca_3(PO_4)_2$, occurs in bone and in modified form in some mineral deposits. Its chief use is in fertilizers and in the manufacture of phosphorus and its compounds. It is insoluble in water, but soluble in dilute acids.

Calcium Hypophosphite, $Ca(PH_2O_2)_2$, is used in medicine.

Calcium Chloride, $CaCl_2$, is obtained by acting on the carbonate with hydrochloric acid:—

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2.$$

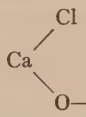
It is very soluble in water. It has a powerful affinity for water, and is used for drying gases.

Calcium Hypochlorite, Bleaching Powder, Chlorinated Lime.—This is produced by passing chlorine into slaked lime, keeping the mixture cool.

The exact composition of the commercial bleaching powder is undetermined; it contains some unchanged calcium hydroxide, and exhibits the reactions of a mixture having the formula—

$$Ca(ClO)_2 + CaCl_2,$$

but is considered by some to be more accurately expressed by the formula—



Bleaching powder, when in good condition, is a loose, dry, white powder, with a faint and not disagreeable odor. If it smells of chlorine it is in bad condition. It dissolves in water. The solution possesses strong bleaching and disinfecting powers, for which purposes it is largely used. Acids, even carbonic acid, decompose it, setting chlorine free. It is generally, but erroneously, called *chloride of lime*.

Calcium Fluoride, CaF_2, is found as the mineral, *Fluor Spar*. Small quantities exist in bones and teeth.

BARIUM

Barium, Ba, 137.4, occurs naturally as sulphate and carbonate. It is a moderately heavy, pale yellow, easily oxidized solid.

Barium Oxide, Baryta, BaO, easily takes up water, forming barium hydroxide, BaH_2O_2, which is soluble in water.

Barium Peroxide, BaO_2, is used in making hydrogen peroxide.

Barium Carbonate, $BaCo_3$, is found in nature as *witherite.* It is nearly insoluble in water.

Barium Sulphate, $BaSO_4$, *Barytes, Heavy Spar,* is found abundantly as *gangue,* that is, rock surrounding metallic veins. It is heavy, white, and insoluble in water. It is used as a substitute and adulterant for white lead, and also as a source of the other barium salts.

Barium Nitrate, $Ba(NO_3)_2$, is used in making green fire.

Barium Chloride, $BaCl_2$, is used as a test solution for sulphates.

Barium communicates to flame a yellowish-green color. Sulphuric acid and sulphates produce in barium solutions a white precipitate of barium sulphate, insoluble in acids or alkalies.

STRONTIUM

Strontium, Sr, 87.6, resembles barium in its compounds and chemical relations. It occurs naturally as sulphate and carbonate.

Strontium Nitrate is used in making red fire.

Strontium compounds give to flame a crimson tint. Its solutions produce with sulphuric acid a white precipitate resembling that given by barium.

RADIUM

Radium, Ra, 227.—This exists in minute amount in some minerals. It is, however, widely distributed and has been detected in some natural waters. Only a few compounds, have been prepared. These compounds emit without appreciable loss of weight several forms of material emanations as well as heat, so that it is a constant source of energy. Radium undergoes spontaneous decomposition by which helium is formed and a gaseous substance which was at first called "radium emanation" then "niton" (Nt) and now "radon" (Rn). Radon has an approximate atomic weight of 222 and its atomic number is 86. It has the characteristics of a member of the argon (zero valency) group. Radon decomposes into helium and a new form of radium. These phenomena are examples of transformations of the elements. The properties of radium compounds are designated as radio-activity, and some radio-activity is communicated to other substances in contact with radium compounds.

MAGNESIUM

Magnesium, Mg, 24.3, occurs as a carbonate (*magnesite*), silicate (*talc* and *soapstone*), also as hydroxide and chloride. Most natural waters contain magnesium compounds. It is a bright, malleable solid. Sp. gr., 1.74. When strongly heated in the air it burns with a bright light, producing MgO. Magnesium compounds cause *hardness* in water similar to that produced by calcium salts.

Magnesium Oxide, MgO, *Magnesia*, is a light, white powder, insoluble in water, and neutralizing acids.

Magnesium Carbonate, $MgCO_3$, occurs as a mineral (*magnesite*). The artificial form, known as *magnesia alba*, is an oxycarbonate.

Magnesium Sulphate, $MgSO_4$, forms colorless crystals, having the composition $MgSO_4$, $7H_2O$, *Epsom Salt*. It is very soluble in water.

Magnesium Chloride, $MgCl_2$, resembles zinc chloride in some respects, but does not have the same corrosive action. When mixed with magnesium oxide it sets to a hard mass.

ZINC

Zinc, Zn, 65.4, exists as sulphide (*blende*), carbonate (*calamine*), silicate (*electric calamine*), and as oxide. It is hard, bluish-white, generally decidedly crystalline. Sp. gr., 7.14. It melts at 770° F. (410° C.), and distils at about a red heat. It is brittle at ordinary temperatures. When highly heated it burns with a greenish-white flame, producing ZnO. Acids and strong alkalies dissolve it. It is employed in making several important alloys, as brass and gun-metal, which contain copper and zinc, and German silver, which contains copper, zinc and nickel. *Galvanized iron* is simply iron covered with a layer of zinc by dipping it in a bath of melted zinc. Commercial zinc often contains arsenic.

Zinc Oxide, ZnO, *Zinc White*, is a soft powder, yellow when hot, white when cold. It is used as a paint, as an application in surgical dressings, and as a face powder.

Zinc Hydroxide, ZnH_2O_2, is a white body, soluble in acids and alkalies.

Zinc Sulphate, $ZnSO_4$, *White Vitriol*, forms white crystals having the formula $ZnSO_4$, $7H_2O$. They are soluble in water, and an emetic.

Zinc Chloride, $ZnCl_2$, forms white masses, which absorb water rapidly from the air (*deliquesce*) and make a strong solution. Zinc chloride is a powerful corrosive, coagulates albuminous matter, and is used as a preservative in anatomical preparations, also as an application in dentistry.

When a strong solution is mixed with zinc oxide, a hard, white, insoluble mass is soon formed. This is termed *oxychloride*.

A white precipitate of zinc sulphide is thrown down by the action of hydrogen sulphide on alkaline solution of zinc salts.

Cadmium, Cd, 112.3, occurs in zinc ores. It is silver-white and crystalline. Sp. gr., 8.6. It melts at 442° F. (228° C.), and is nearly as volatile as mercury. It is easily dissolved by ordinary acids. *Cadmium Sulphide*, CdS, is obtained as an orange-yellow precipitate by passing hydrogen sulphide into solutions of cadmium compounds.

MERCURY

Mercury, Hg, 200.6.—This metal is found native, and as sulphide (cinnabar). It is liquid at the ordinary temperature, freezing at −40° F. and C., and boiling at 675° F. (357° C.); When pure it does not tarnish in dry or moist air, but above 300° C. it absorbs oxygen. It is very lustrous and heavy; specific gravity, 13.56. Combinations of mercury with other metals are known as *amalgams*. These are soft or hard, according to the quantity of mercury used. Two series of salts are known, corresponding to the copper salts, and called respectively *mercurous* and *mercuric* salts.

Mercuric Oxide, HgO, *Red Precipitate* is a red or yellowish-red powder. It is an active base.

Mercuric Sulphate, $HgSO_4$, is a white powder, which is decomposed by water, forming a yellow oxysulphate, $HgSO_4$, $2HgO$, called *turpeth mineral*.

Mercuric Nitrate, $Hg(NO_3)_2$, is generally seen in solution with excess of nitric acid, forming the *acid mercury nitrate* used in medicine.

Mercuric Chloride, $HgCl_2$, *Corrosive Sublimate*, is a heavy, white, crystalline powder, soluble in water and ether, and having an acrid, metallic taste. It is very poisonous. It forms with albumin an insoluble precipitate. Dilute solutions of mercuric chloride are now much used as an antiseptic in surgery.

Mercuric Iodide, HgI_2, *Red Iodide*, is formed when mercuric chloride is mixed with potassium iodide:—

$$HgCl_2 + 2KI \rightarrow HgI_2 + 2KCl.$$

It is at first yellow, but changes to a brilliant scarlet.

Mercuric Sulphide, HgS, *Vermilion, Cinnabar*, is an important ore of mercury.

Few of the *Mercurous Salts* are of importance.

Mercurous Oxide, Hg_2O, is a black powder, easily decomposed.

Mercurous Chloride, HgCl, *Calomel*, is a white, heavy, tasteless powder, insoluble in water.

Mercuric salts give with potassium iodide a yellow precipitate of HgI_2, changing to scarlet and soluble in excess of the precipitant.

Any compound containing mercury will give with Reinsch's test (see under "Arsenic") a bright, silvery coating on copper foil, easily driven off by heat and condensing as opaque globules.

TIN

Tin, Sn, 119, occurs principally as a dioxide, called *tin-stone*. The element is white, soft and easily beaten into foil, but is not tough; sp. gr., 7.28. It fuses at 442° F. (228° C.), and resists very well the action of the air and of cold acids. Nitric acid forms a dioxide which immediately takes up water and forms an acid. Tin forms several valuable alloys—pewter, gun-metal, type-metal, bronze and solder. Speculum metal, used for metal mirrors, is an alloy of copper and tin; glass mirrors are coated with an amalgam of tin. Tin plate is iron coated with tin by dipping it into a bath of the melted metal. Two series of salts are known—*stannous*, unsaturated, and *stannic*, saturated.

Stannous Oxide, SnO, is a feeble base.

Stannous Chloride, $SnCl_2$, is formed by dissolving tin in hydrochloric acid. Stannous chloride is used as a reducing agent. When mixed with mercuric chloride, mercury is set free and stannic chloride formed:—

$$HgCl_2 + SnCl_2 \rightarrow Hg + SnCl_4.$$

Stannic Oxide, SnO_2, *Stannic Anhydride*, is found as a mineral; it is also produced by burning tin in the air, by oxidizing it with nitric acid and by adding an alkali to stannic chloride. It unites with water in various proportions to form acids, and these form salts called stannates and metastannates.

Stannic Chloride, $SnCl_4$, *Tin Tetrachloride, Libavius' Fuming Liquor*.—This body is largely used by dyers under the name of *nitro-muriate of tin*. It is a colorless fuming liquid, boiling at 239.5° F. (115.3° C.).

Stannic Sulphide, SnS_2, *Mosaic Gold*, is a bronze-colored powder used in printing and coloring.

LEAD

Lead, Pb, 207.2, occurs as sulphide (*galena*), carbonate, sulphate and phosphate. Its chemical functions ally it with several groups. It is

generally a dyad. Its sulphate is nearly insoluble in water, which connects with the barium group. It shows tetrad valency which connects it with the carbon group, and it has also some resemblances to silver.

Lead is a soft solid, but resists well the action of air and of some strong acids, for which reason it is used in constructing chemical apparatus. Pure water, free from air, has little action on lead, but aërated water oxidizes and dissolves this oxide in small quantity. Phosphates, carbonates and silicates interfere with this action, because they precipitate insoluble lead compounds. Lead melts at 617° F. (325° C.). Sp. gr., 11.5.

Some important alloys are: *Type-metal*, containing lead and antimony; *solder*, about equal parts of lead and tin; *pewter*, 1 part lead and 4 parts tin.

Lead Monoxide, PbO, *Litharge*, *Massicot*, is a yellowish or reddish powder, slightly soluble in water and neutralizing the most powerful acids. It fuses at a red heat, and in this condition combines easily with silica, for which reason it is often used in glazing cheap earthenware.

Lead Dioxide, PbO_2, *Puce*, is a brown powder, insoluble in water. It may be regarded as the anhydrid of plumbic acid, H_4PbO_4.

Red Lead, *Minium*, usually Pb_3O_4.—It forms a bright powder, not constant in composition.

Lead Sulphide, PbS, is abundant as a mineral, *galena*, forming large, cubical, lead-colored crystals. It can be formed by adding hydrogen sulphide to lead solutions.

Lead Carbonate, $PbCO_3$, occurs as a mineral, but is made artificially on a very large scale for use in paints. The *white lead* of commerce is an hydroxy salt of varying composition, approximately $2PbCO_3 + PbH_2O_2$.

Lead Sulphate, $PbSO_4$, is a white insoluble powder, produced by adding sulphates to lead solutions.

Lead Chloride, $PbCl_2$, forms slender crystals, not very soluble in cold water.

Lead Iodide, PbI_2, yellow crystalline powder, sparingly soluble in cold water.

Lead Chromate, $PbCrO_4$, *Chrome Yellow*, is described under chromium.

ANTIMONY

Antimony, Sb, 120, occurs sometimes in the free state, but generally as sulphide, Sb_2S_3. It is also called *Stibium*.

Antimony is bluish-white, brittle, generally high crystalline and of brilliant luster. It fuses at 842° F. (450° C.), and volatilizes at a red

heat. On cooling from the melted condition it expands somewhat, and some of its alloys retain this property, for which reason it is used in type metal and other alloys which must take sharp casts. Like arsenic, it is not soluble in any simple solvent.

The chemical relations of antimony are much like those of arsenic, phosphorus and nitrogen. It forms an oxide which is slightly basic.

Antimony is detected by tests similar to those of arsenic. The distinctive differences are:—

1. The sublimate of free antimony cannot be obtained by the reduction test unless a very high temperature be used.

2. Antimonous oxide cannot be volatilized except by a high heat, and does not usually form octahedral crystals, but these have been obtained under certain conditions.

3. The copper slip in Reinsch's test becomes covered with a bluish or violet deposit, which gives a sublimate only with great difficulty.

4. In Marsh's test a much darker spot is obtained; it is volatilized with difficulty, and not dissolved by a solution of bleaching powder.

5. The liquid tests give no result, except with hydrogen sulphide, which produces an *orange-red* precipitate of antimonous sulphide, Sb_2S_3.

Stibine, Hydrogen Antimonide, SbH_3, resembles the corresponding arsenic compound, and is produced under similar conditions.

Compounds of Antimony with Oxygen.—These are:—

Sb_2O_3.....Antimonous oxide, or anhydride.
Sb_2O_5.....Antimonic " "

Antimonous Oxide, Sb_2O_3.—This is found as a mineral, and is also readily prepared by burning antimony in the air. It is like As_2O_3 in many of its chemical relations, but is insoluble in water, less volatile, and shows some power of reacting with acids to form salts. When boiled with a solution of cream of tartar (acid potassium tartrate) antimonous oxide loses one atom of oxygen, and dissolves, forming *tartar emetic*, potassium antimonyl tartrate. This compound is the most familiar preparation of antimony, as it dissolves in water without decomposition. The reaction in its production is:—

$$2KHC_4H_4O_6 + Sb_2O_3 \rightarrow 2K(SbO)C_4H_4O_6 + H_2O.$$

The SbO replaces the hydrogen.

Antimonic Oxide, Sb_2O_5, forms acids corresponding to the meta- and pyrophosphoric acids: $HSbO_3$, metantimonic, and $H_4Sb_2O_7$, pyranti-

monic acid. Pyrantimonic acid is remarkable for forming a sodium compound sparingly soluble in water.

Antimony forms compounds with chlorine, bromine and iodine analogous to those of phosphorus and arsenic. They are mostly hydrolyzed when mixed with large quantities of water, yielding at first an oxycompound, finally an oxide. With antimonous chloride the reactions are:—

$$SbCl_3 + H_2O \rightarrow SbOCl + 2HCl.$$

The oxychloride becomes, by further action of water, converted into antimonous oxide:—

$$2SbOCl + H_2O \rightarrow Sb_2O_3 + 2HCl.$$

Antimony Sulphides.—Two are known:—

Sb_2S_3.....Antimonous sulphide.
Sb_2S_5.....Antimonic sulphide.

Antimonous Sulphide is the principal ore of antimony. It is found as a shining, gray, crystalline mass, fusible and easily oxidized by heating in the air. Hydrochloric acid dissolves it easily, forming antimonous chloride and hydrogen sulphide:—

$$Sb_2S_3 + 6HCl \rightarrow 2SbCl_3 + 3H_2S.$$

On the other hand, a current of hydrogen sulphide passed into antimony solutions produces the antimonous sulphide as an *orange-red* precipitate.

Antimonic Sulphide is an orange-yellow body.

The chemical relations of antimony are well shown in its sulphides. Both of them act as anhydrides and form a series of salts.

$KSbS_2$.....Potassium sulphantimonite.
or " thioantimonite.

is strictly comparable to

KNO_2.....Potassium nitrite.

Antimonic sulphide forms salts upon the pattern of the orthophosphates.

Na_3SbS_4.....Sodium sulphantimonate.
or " thioantimonate.

is analogous to

Na_3PO_4.....Sodium orthophosphate.

Sodium thioantimonate has been used in photography under the name of *Schlippe's salt.*

BISMUTH

Bismuth, Bi, 209, is commonly found native; also as oxide and sulphide. It is hard, brittle, reddish-white and distinctly crystalline. It fuses at 507° F. (264° C.), expanding when it solidifies. It is not much affected by the air. Nitric acid dissolves it.

Bismuth Sesquioxide, Bi_2O_3, the only important oxide, is obtained as a yellowish powder, by burning bismuth in the air or by heating the carbonate or nitrate. It acts as a base.

Bismuth Nitrate, $Bi(NO_3)_3$, made by dissolving bismuth in nitric acid, is a soluble, white, crystalline mass. When added to a large volume of water, a white precipitate of bismuth oxynitrate, of irregular composition, but approximating $BiNO_3O$, is thrown down. This powder, ordinarily called *bismuth subnitrate,* is used in medicine and sometimes as a cosmetic. When it is boiled with sodium hydroxide and a solution of dextrose, a heavy black powder of free bismuth is formed.

Bismuth Chloride, $BiCl_3$, is decomposed by water in a manner similar to the nitrate, producing an oxychloride.

Bismuth Subcarbonate, more properly oxycarbonate, approximating to the formula, $BiOCO_3$, but variable in composition, is used in medicine.

Vanadium, V, 51, is a rare body, found chiefly in combination with iron and lead. It forms four oxides. VO, V_2O_3, VO_2, V_2O_5.

Vanadic Anhydride, V_2O_5, forms salts called vanadates. Lead vanadate is found as a mineral. It yields compounds analogous to metaphosphoric acid, and also forms salts with some of the strong acids. Vanadium has acquired importance from its use in steel.

NOTE IN REGARD TO THE IRON GROUP

The group next to be considered, conveniently termed the "iron-group" from its most important member, offers some difficulty because the compounds seem to be derived from elements exhibiting diad and triad valencies, thus constituting an exception to the rule that valencies change by two degrees. The exception has been regarded by many chemists as apparent rather than real, and the explained by the supposition that in the higher valency the atoms are united in pairs, with consequent loss of one degree of valency in each. A discussion of this view and a graphic representation of the supposed arrangement will be found on p. 14. The present tendency is to divide these formulas whenever practicable, writing $FeCl_3$, for example, instead of Fe_2Cl_6. In many cases, such as

Fe_2O_3, the division cannot be made. In this work, the divided formulas will be used in deference to general custom, but the method has no particular advantage.

ALUMINUM

Aluminum, Al, 27, is abundant as silicate, in clay and many common rocks. Many building materials are mixtures of aluminum silicate with other silicates.

Aluminum is white but not very lustrous, malleable and ductile, sonorous and very light; sp. gr., 2.6. It tarnishes slightly in the air, and dissolves rapidly in hydrochloric acid and in sodium hydroxide, but not so readily in sulphuric or nitric acid. It melts at 840° F. (450° C.). Valuable alloys of aluminum with copper, nickel, silver, etc., are now made. The alloy of 90 parts of copper with 10 parts aluminum has the color of gold.

Only one series of aluminum compounds is important. These possess many analogies to the higher series of iron salts; hence, they may be regarded as forming compounds by the joint action of two tetrad atoms, which act as a hexad.

Aluminum Oxide, Al_2O_3, occurs naturally as *corundum*, which, when crushed, constitutes *emery;* finely crystallized, as the *ruby*, *sapphire* and *emerald*. It can be prepared by heating ammonium alum; it then forms a white powder. In all the anhydrous forms it is absolutely insoluble in water, and almost so in acids and alkalies.

Aluminum Hydroxide, AlH_3O_3, or $Al_2H_6O_6$, is a gelatinous white mass, easily soluble in acids and alkalies. It has a strong affinity for organic matter; with organic colors it forms precipitates called lakes. The affinity of aluminum hydroxide for organic matter is utilized in the filtration of water. A small amount of some aluminum compound, usually aluminum sulphate, is dissolved in the water. This reacts with the carbonates which are generally present (calcium, magnesium or sodium carbonates) to form aluminum hydroxide with evolution of a carbon dioxide (see p. 72). The aluminum hydroxide combines with the organic matter, and being a flocculent mass, can be removed easily by filtration. The process permits of rapid filtration. The aluminum compound is usually called the "coagulant."

Aluminum Sulphate, $Al_2(SO_4)_3$, is now largely used in dyeing and in other operations. It forms a white crystalline mass having an acid reaction.

Alums.—The alums are a series of double sulphates. One alum has the formula—

$$AlK(SO_4)_2,12H_2O.$$

The aluminum in this compound may be replaced by most of the elements of the iron group. The potassium may be replaced by any element of its group, or by ammonium, giving a series of salts of which the following are examples:—

$AlK(SO_4)_2,12H_2O$.....Potassium alum.
$CrNa(SO_4)_2,12H_2O$.....Chromium sodium alum.
$Fe(NH_4)(SO_4)_2,12H_2O$.....Ferric ammonium alum.

All these may be written with double formulas; see pp. 12 and 14.

These compounds contain the same amount of water of crystallization and all crystallize in octahedra. Bodies giving rise to compounds similar both in composition and in crystalline form are called *isomorphous.*

Common Alum is either potassium alum or ammonium alum. It dissolves easily in water, the solution being sour and astringent.

When alum crystals are gently heated they swell up, lose part or all of their water of crystallization, and fall to a white powder—burnt alum.

Aluminum Chloride, $AlCl_3$, is prepared by heating alumina and charcoal in a current of chlorine:—

$$Al_2O_3 + 3C + 6Cl \rightarrow 3CO + 2AlCl_3.$$

Glass Pottery and Porcelain.—These are mostly mixtures of aluminum, calcium and sodium silicates. Colored glasses are produced by the use of various oxides.

Pottery and earthenware are made of clay, glazed with a fusible sodium silicate. Lead silicate is also used. Porcelain is a mixture of feldspar (aluminum-potassium silicate), sand and *kaolin,* a hydrated aluminum silicate.

IRON

Iron, Fe, 55.8, occurs as oxide, sulphide and carbonate; its compounds occur in small quantities in many rocks and soils; it is taken up by plants; and is an essential constituent of the blood of the higher animals. It sometimes occurs native, especially in meteoric stones. A fine grade, Quevenne's iron, for use in medicine, is made by the action of hydrogen on the sesquioxide. On the large scale, iron ore, which generally consists of an oxide or carbonate mixed with clay, sand and other minerals, is heated in blast furnaces with coal and limestone. The limestone makes a

fusible calcium silicate, *slag;* the coal takes the oxygen away from the iron. The melted mass is then run out into thick bars, forming *pig* or *cast iron*, containing 4 or more per cent. of carbon, also phosphorus, sulphur, silicon and other bodies.

Wrought iron contains but little carbon. The steel used for tools contains about 1% of carbon; it is, therefore, intermediate in composition. The structural steel now so much used for buildings, bridges and railroad tracks contains more than 1% of carbon. Pure iron is very soft, but commercial iron has many impurities which give special qualities; carbon gives hardness and fusibility; phosphorus and sulphur give fusibility and great brittleness, and are objectionable. Cast iron melts at about 3000° F. (1649° C.). Many alloys of iron are now made for armor-plate, cannon, projectiles, automobile parts and other important constructions.

Iron is strongly magnetic and not much affected by dry air, but is oxidized by moist air and easily dissolved by acids. It forms two series of salts—*ferrous*, in which it is a dyad, and *ferric*, in which it is apparently a triad, but the formulas of the ferric compounds may be doubled and the iron regarded as a double atom:—

Dyad iron	Hexad iron
—Fe—	≡Fe—Fe≡

Ferrous salts are generally green; ferric salts brown or red.

Ferrous salts are converted into ferric by oxidizing agents. If the ferric salts are written with double formulas, the reaction will always require two molecules of ferrous for one of ferric; thus—

$$2FeO + O \rightarrow Fe_2O_3.$$
$$2FeCO_3 + O \rightarrow Fe_2O_3 + 2CO_2.$$

To make a normal ferric salt one-half as much of the negative element as the ferrous salt already contains must be added; that is, one molecule of the radical for every two molecules of the ferrous salt. In making ferric chloride, the complete reaction is—

$$6FeCl_2 + 6HCl + 2HNO_3 \rightarrow 6FeCl_3 + 4H_2O + 2NO.$$

Ferrous salts are formed from ferric by the action of reducing agents, especially powdered zinc, nascent hydrogen or sulphurous acid. With ferric chloride and zinc the reaction is—

$$2FeCl_3 + Zn \rightarrow 2FeCl_2 + ZnCl_2.$$

Hydrogen sulphide will also reduce ferric salts:—

$$2FeCl_3 + H_2S \rightarrow 2FeCl_2 + 2HCl + S.$$

Ferrous Hydroxide.—Ferrous hydroxide, FeH_2O_2, is formed as a precipitate by the action of alkaline hydroxides upon a ferrous salt. It immediately begins to change by absorbing oxygen, and becomes ferric hydroxide.

Ferric Oxide, Fe_2O_3, *Red Oxide, Sesquioxide*, occurs frequently in small amounts in many minerals, and also as iron ore, called *red hematite* or *specular iron*. It may be prepared artificially by heating ferrous sulphate ($2FeSO_4 \rightarrow 2Fe_2O_3 + SO_2 + SO_3$), and is the residue obtained in making Nordhausen sulphuric acid. It is a soft, red powder, difficult to dissolve in acids. The finger grades constitute *rouge;* the coarser, *venetian red* and *crocus*, are used for paints.

Ferric Hydroxide, FeH_3O_3 or $Fe_2H_6O_6$, is easily formed by adding an alkaline hydroxide to a ferric salt:—

$$2FeCl_3 + 6KHO \rightarrow 6KCl + 2FeH_3O_3.$$

Ferric hydroxide is a soft, brown mass, insoluble in water, but dissolving easily in acid. It has been used as an antidote to arsenous oxide (arsenic), for which use it must be freshly prepared. Ordinary iron rust consists of impure ferric hydroxide and it also occurs in an impure condition as *brown hematite.*

Magnetic Iron Oxide, Fe_3O_4, is found as a finely crystallized mineral and valuable ore of iron. It can retain magnetism, and is occasionally found in a magnetized condition.

Ferrous Sulphide, FeS, made by fusing iron with sulphur, is a dark, slag-like mass, used as a source of hydrogen sulphide.

Iron Pyrites.—Several sulphides, especially the disulphide, FeS_2, occur abundantly as minerals. They form bright brass-colored crystals and are often mistaken for gold, hence called *fool's gold.* They are of no use as iron ores, on account of the sulphur, but are used as a source of sulphuric acid. For this purpose they are heated in a free supply of air, by which most of the sulphur is burned and forms sulphur dioxide.

Ferrous Carbonate is a valuable iron ore and exists in many natural waters. It is produced by mixing ferrous sulphate with sodium carbonate:—

$$FeSO_4 + Na_2CO_3 \rightarrow FeCO_3 + Na_2SO_4.$$

In this form, however, and also as dissolved in water, it is prone to oxidation, passing into the condition of ferric hydroxide, which forms a red deposit. This oxidation is hindered by presence of sugar. The carbonate occurring naturally in the crystallized form is permanent in

the air. Waters containing iron compounds in appreciable amount are termed *chalybeate.*

Ferrous Sulphate, $FeSO_4$, *Green Vitriol, Copperas,* is formed by dissolving iron in sulphuric acid or by oxidizing iron pyrites by exposing them in a moist condition to air. It forms clear green crystals containing $FeSO_4,7H_2O$, easily soluble in water, the solution being liable to oxidation.

Ferric Sulphate.—An oxysulphate, called *Monsel's Salt,* or when dissolved *Monsel's Solution,* is used as a styptic.

Ferric Chloride, $FeCl_3$, is generally used in alcoholic solution, sometimes called *muriated tincture of iron.* Ferric chloride is made by boiling ferrous chloride with nitric acid and hydrochloric acid:—

$$6FeCl_2 + 6HCl + 2HNO_3 \rightarrow 6FeCl_3 + 4H_2O + 2NO.$$

When the solution is evaporated a red crystalline mass of $FeCl_3 + 3H_2O$ is formed, which is freely soluble in water and alcohol.

Ferrous salts are usually green; ferric red or brown.

The two classes of iron salts can be easily distinguished by certain tests:—

	With ferrous salts	With ferric salts
Ammonium hydroxide,	Green ferrous hydroxide, turning red,	Red ferric hydroxide.
Potassium ferrocyanide,	Light blue precipitate,	Dark blue precipitate.
Potassium ferricyanide,	Dark blue precipitate,	No precipitate.
Tannin,	No action,	Black precipitate.
Potassium thiocyanate,	No action,	Blood red color, but no precipitate.

MANGANESE

Manganese, Mn, 55, exists principally as oxide, also as sulphide, carbonate and silicate. It is grayish-white, brittle, and hard; specific gravity between 7 and 8. It forms two series of salts parallel to those of iron.

Manganous Oxide, MnO, and *Hydroxide,* MnH_2O_2, absorb oxygen rapidly.

Manganous Chloride, $MnCl_2$, forms pink crystals, deliquescent and soluble in water.

Manganous Sulphate, $MnSO_4,7H_2O$, is a rose-colored salt, soluble in water.

Manganese Dioxide, MnO_2, *Black Oxide*.—This is an abundant mineral. It is extensively used as an oxidizing agent and in the manufacture of chlorine. Ordinarily it is in black masses or powder.

Manganese Acids.—Manganese furnishes two acids.

H_2MnO_4 ..... Manganic acid.
$HMnO_4$ ..... Permanganic acid.

The former has not been obtained, but some of its salts are known.

Manganates.—These are formed by fusing manganese dioxide with potassium hydroxide and potassium nitrate or chlorate. Potassium manganate, K_2MnO_4, is formed as a green crystalline mass. When dissolved in water the manganates turn into permanganates by the following reaction:—

$$3K_2MnO_4 + 2H_2O \rightarrow 2KMnO_4 + MnO_2 + 4KHO.$$

The change of composition is indicated by a change of color from green to red for which reason crude potassium manganate is sometimes called *chameleon mineral*.

Potassium Permanganate, $KMnO_4$, is much used as an oxidizing and deodorizing agent. The solution is decomposed by organic matters, by sulphites and sulphides and reducing agents generally, becoming converted into a colorless solution. It can therefore be employed not only to destroy organic matter, but often as an approximate measure of the amount present.

CHROMIUM

Chromium, Cr, 52, occurs principally as an oxide in combination with iron, constituting chrome iron ore, $FeCr_2O_4$; also as lead chromate, $PbCrO_4$. The element resembles iron but is not so easily oxidized or dissolved. It forms two sets of salts, analogous to those of iron, and also anhydrides. The compounds in which it acts as a positive are of very little importance. The chromous salts are unstable. Almost all the chromium compounds are highly colored.

Chromic Oxide, Chromium Sesquioxide, Cr_2O_3, *Chrome Green*, is a bright green powder used as a paint.

Chromic Anhydride, CrO_3, forms bright red crystals, very deliquescent, soluble in water, and having powerful oxidizing properties.

Potassium Chromate, K_2CrO_4, forms lemon-yellow crystals soluble in water.

Potassium Dichromate, $K_2Cr_2O_7$, commonly known as *bichromate*, is in large, bright red crystals soluble in water. It is extensively used as a source of mineral colors. It may be regarded as a salt of dichromic acid, $H_2Cr_2O_7$, produced by subtracting one molecule of water from two molecules of chromic acid:—

$$2H_2CrO_4 - H_2O \rightarrow H_2Cr_2O_7.$$

Lead Chromate, Chrome Yellow, $PbCrO_4$, easily formed by adding a soluble chromate to a lead compound:—

$$Pb(NO_3)_2 + K_2CrO_4 \rightarrow PbCrO_4 + 2KNO_3.$$

It is bright yellow and insoluble in water. Commercial chrome yellow often contains white lead and chalk.

A mixture of potassium dichromate and sulphuric acid is used as an oxidizing agent. The chromic acid becomes reduced and forms chromic sulphate; the liquid turns green, and afterward deposits dark, ruby-red crystals of chrome alum—

$$CrK(SO_4)_2,12H_2O.$$

Chromates are recognized by their color and by the yellow precipitate of lead chromate formed when mixed with lead salts.

NICKEL

Nickel, Ni, 58.7, occurs principally in union with arsenic and sulphur; also in meteoric iron as an alloy. It is hard and white, of specific gravity 8.8, fusing at a high temperature and resisting the action of air at common temperatures. Like iron, it can acquire permanent magnetism. An alloy of copper, zinc and nickel is called German silver.

The "nickel" coin of the United States contains copper and nickel.

Nickel Monoxide, NiO, and *Hydroxide*, NiH_2O_2, are green and form green salts.

Nickel Sulphate, $NiSO_4$, is the most important salt. It usually crystallizes with seven molecules of water

Cobalt, Co, 58, is found associated with nickel, which it closely resembles in properties and chemical relations. Its compounds are mostly red or blue. The element itself is hard, white, magnetic and difficult to fuse; specific gravity, 8.7. The oxides, sulphates, carbonates, etc., resemble in composition those of nickel. Cobalt salts are mostly bright red.

PLATINUM

Platinum, Pt, 195.2, occurs native, also alloyed with gold and silver and other elements.

Platinum is hard, white and very heavy; specific gravity, 21.5; it fuses only at a very high temperature. It resists perfectly the action of the air and of most chemical agents, and for this reason is largely used in chemical operations. It dissolves in hot *aqua regia*, forming *platinum tetrachloride, platinic chloride*, $PtCl_4$. Platinum forms two series of compounds; its oxides are only feebly basic.

Most platinum compounds are decomposed by moderate heating, the element being set free in a porous condition commonly called "platinum sponge." This has power to absorb some gases, especially oxygen, and thus bring about combination. Cold platinum sponge introduced into a mixture of hydrogen and oxygen will quickly become red hot and ignite the mixture. Sulphur dioxide and air passed through the sponge at a temperature of 100° C. (212° F.) forms sulphur trioxide, a reaction that does not occur when the mixture alone is heated. This reaction is utilized in the manufacture of sulphuric acid (see p. 60).

By reducing platinum compounds with zinc, or formic acid, a more finely divided material, termed "platinum black" is obtained. This has still higher power of absorption.

Platinum Tetrachloride.—Platinic Chloride, $PtCl_4$, is in brownish-red crystals. It forms insoluble precipitates with potassium and ammonium, but not with sodium, and is of much use in analysis for the separation of potassium for sodium.

Rare Elements

Most of the remaining elements are rare and have as yet few applications of moment. Their names, symbols and accepted atomic weights are given in the table of elements (page 101). Great scientific interest attaches to some of them, and in a few cases their compounds are used in special tests.

The mantles used for incandescent gas lights are composed of thorium dioxide ThO_2, with a little cerium sesquioxide Ce_2O_3. Thorium exhibits radioactivity and a highly radio-active substance "mesothorium" has been separated from it. Many of the rare elements are widely distributed in minute amount. In fact, as the methods of research increase, and,

especially as delicate methods of testing are discovered, a general distribution of all the elements is indicated. An alloy of cerium and iron is pyrophoric, that is, yields sparks when rubbed. It is used for gas-lighters.

Helium deserves special notice on account of the somewhat romantic history of its discovery and subsequent uses. In 1868, Lockyer, a British astronomer, observing a total eclipse in India, noticed in the spectrum of the sun a yellow line near, but not identical with that of sodium, and not referable to any known element. He inferred that this was due to an element existing in the sun which had not been found on the earth, and called it provisionally "helium" from the Greek word for "sun." For a long while this indirect knowledge was all that had been obtained, but small amounts of helium were detected in some minerals and later notable quantities were found in the natural gas in the southwestern part of the United States. As helium is only twice as heavy as hydrogen and is incombustible, its value for filling balloons was at once recognized. As a result of research, the United States military authorities have been able to secure very large amounts of helium which are used in filling dirigibles. It is somewhat unfortunate that Lockyer assumed that the element was a metal and gave it a name terminating in "um." The name should be "helion," to agree with the other elements of this group which is the so-called "zero" group or "noble" gases, which have no chemical affinity.

Elements, Symbols and Atomic Weights

Aluminum	Al	27.0	Mercury	Hg	200.61
Antimony	Sb	120.0	Molybdenum	Mo	96.0
Argon	A	39.9	Neodymium	Nd	144.3
Arsenic	As	74.96	Neon	Ne	20.2
Barium	Ba	137.37	Nickel	Ni	58.68
Bismuth	Bi	209.0	Nitrogen	N	14.01
Boron	B	10.8	Osmium	Os	190.8
Bromine	Br	79.9	Oxygen	O	16.00
Cadmium	Cd	112.41	Palladium	Pd	106.7
Calcium	Ca	40.0	Phosphorus	P	31.03
Carbon	C	12.00	Platinum	Pt	195.2
Cerium	Ce	140.25	Potassium	K	39.10
Cesium	Cs	132.81	Praseodymium	Pr	140.9
Chlorine	Cl	35.46	Radium	Ra	226.96
Chromium	Cr	52.0	Radon	Rn	222.0
Cobalt	Co	58.94	Rhenium	Re	187.0
Columbium	Cb	93.1	Rhodium	Rh	102.9
Copper	Cu	63.57	Rubidum	Rb	85.45
Dysprosium	Dy	162.5	Ruthenium	Ru	101.7
Erbium	Er	167.7	Samarium	Sa	150.4
Europium	Eu	152.0	Scandium	Sc	45.1
Fluorine	F	19.0	Selenium	Se	79.2
Gadolinum	Gd	157.3	Silicon	Si	28.06
Galium	Ga	69.7	Silver	Ag	107.88
Germanium	Ge	72.6	Sodium	Na	23.00
Glucinum	Gl	9.0	Strontium	Sr	87.63
Gold	Au	197.2	Sulphur	S	32.07
Hafnium	Hf	180.8	Tantalum	Ta	181.5
Helium	He	4.0	Tellurium	Te	127.5
Holmium	Ho	163.4	Terbium	Tb	159.2
Hydrogen	H	1.008	Thallium	Tl	204.4
Illinium	Il		Thorium	Th	232.15
Indium	In	114.8	Thulium	Tm	169.4
Iodine	I	126.93	Tin	Sn	118.7
Iridium	Ir	193.14	Titanium	Ti	48.1
Iron	Fe	55.84	Tungsten	W	184.0
Krypton	Kr	82.91	Uranium	U	238.17
Lanthanum	La	138.9	Vanadium	V	51.0
Lead	Pb	207.20	Xenon	Xe	130.2
Lithium	Li	6.94	Ytterbium	Yb	173.6
Lutecium	Lu	175.0	Yttrium	Yt	88.9
Magnesium	Mg	24.32	Zinc	Zn	65.37
Manganese	Mn	54.93	Zirconium	Zr	91.0
Masurium	Ma	90.0			

DESCRIPTIVE ORGANIC CHEMISTRY

NATURE OF ORGANIC BODIES

Organic chemistry is primarily the study of the substances forming part of the tissues of plants and animals, or produced by the specific action of those tissues. They are very numerous, and by many methods—such as action of heat or powerful chemical agents—new substances may be obtained that are never produced by living organisms, yet these derivatives are also termed "organic." Distinction must be made between "organized" and "organic." Organized bodies have structure, generally cellular, and are produced so far as is known only under the influence of vital action. The term "organic" includes organized and non-organized substances.

For the recognition of organic substances the action of heat usually suffices. It causes decomposition with evolution of smoky odorous vapors. Generally some carbon remains, which can be burned off in a good supply of air. The presence of nitrogen is indicated by the odor of burning wool or flesh. Ammonia is often formed and can be detected by the usual tests. The distinction between the organized and non-organized substances is usually made by the microscope.

Carbon, hydrogen, nitrogen and oxygen are the elements characteristic of organic bodies, but during the last hundred years many substances have been prepared into which mercury, bismuth, arsenic, chlorine or iodine have been introduced; these, although analogous to natural organic substances, are not capable of forming part of healthy tissue. Carbon is present in almost all organic substances, and for this reason organic chemistry has sometimes been called the "chemistry of the carbon compounds." Hydrogen is also almost always present; oxygen frequently; nitrogen less frequently; while sulphur, phosphorus and iron are rather exceptional in their occurrence. The following table gives a list of substances belonging to different classes in organic chemistry, and shows how many changes may be made in the combination of these few elements. The compounds all occur ready formed in nature:—

$C_{10}H_{16}$.....Terpene.
$C_{12}H_{22}O_{11}$.....Cane sugar.
$C_{10}H_{14}N_2$.....Nicotine (from tobacco).
$C_{14}H_{19}NO_3$.....Morphine (from opium).
$C_2H_7NSO_3$.....Taurine (from bile).
$C_3H_9PO_6$.....Glycerophosphoric acid (from brain).
$C_{32}H_{32}FeN_4O_3$.....Hematin (from blood corpuscles).

Proximate and Ultimate Composition.—The tissues of plants and animals, and the immediate products of their decomposition, are generally mixtures of several independent substances. Butter is a mixture of four or five fats; common rosin contains two or sometimes three distinct bodies; opium and Peruvian bark are still more complicated; brain and muscle structures are so complicated that as yet complete analyses have not been made of them. The substances which thus exist naturally in a state of mixture are called *proximate principles*, the separation and identification of them is called *proximate analysis*, and such of them as give characteristic qualities to the articles in which they occur are generally called *active* or *essential principles;* atropine, for instance, is the active principle of belladonna, for although many different bodies are contained in the belladonna leaf, atropine is the one upon which its physiologic principal activity mainly depends. The *ultimate principles* of a substance are the elements (*e. g.*, carbon, hydrogen) which it contains.

Transformation of Organic Bodies.—In addition to the bodies found ready formed in plants and animals, many derivative substances are known. These are produced by many methods, some of which are of general application.

(*a*) Action of Heat.—The great majority of organic compounds are changed by heat, some only slightly, others completely. Many are converted into new bodies, which escape in the condition of vapors, and may be subsequently condensed. In this way coal, when heated, gives rise to gas, tar and pitch, these products being mixtures of many substances. Such a process is called *destructive distillation.*

(*b*) Action of Oxygen.—At high temperatures most organic compounds burn, producing carbon dioxide and water. At low temperatures the oxygen may enter slowly into combination, or, as frequently happens, may substitute the hydrogen, the substitution taking place in the proportion of one atom of oxygen for every two atoms of hydrogen removed In both these actions the resulting bodies are generally acids.

(*c*) Action of Nitric Acid.—This differs with the temperature and concentration. Strong cold acid generally produces a substitution of the molecule NO_2 for H, giving rise to bodies called *nitro-compounds*. When the acid is weak or hot, the action is usually the direct addition of oxygen, according to methods given in the preceding paragraph.

(*d*) Action of Chlorine.—Chlorine sometimes enters into direct combination, but usually displaces the hydrogen and takes its place, atom for atom. Bromine and iodine act in the same manner.

The substituting actions of oxygen, nitric acid, chlorine and similar elements give rise to many important compounds.

(*e*) Hydrolysis.—This is the action of one or more molecules of water in such a manner that the water ceases to exist, its hydrogen and oxygen being distributed in the molecule. Very frequently the group HO (hydroxyl) is produced. Hydrolysis is of frequent occurrence in the processes of putrefaction and fermentation. The action of enzyms is often by hydrolysis, for examples of which see under "Carbohydrates."

(*f*) Dehydrolysis.—Abstraction of hydrogen and oxygen from a molecule in the proportion H_2 to O, with formation of water. This change is often termed "dehydrating," a term that should be limited to removal of water existing as such. In *dehydrolysis*, the water resulting from the reaction does not exist in the original substance. For example, perfectly dry cane sugar, mixed with pure sulphuric acid, is decomposed into carbon and water. Neither substance contains water before mixture. Sulphuric acid and phosphoric anhydride are commonly used as dehydrolyzing agents.

(*g*) So-called Natural Changes.—These are *Fermentation*, *Putrefaction* and *Decay*.

Fermentation and *putrefaction* are similar processes, but it is usual to apply the term putrefaction to the changes which are attended with the evolution of offensive gases and fermentation to those that are not offensive. This difference is dependent mainly upon the difference in the materials that are undergoing change. When these contain much nitrogen and sulphur, the evolved gases are offensive and the action is termed *putrefaction*, but when the compounds contain but little of these elements, the evolved gases are not offensive, and the change is termed *fermentation*. Putrefactions occur, therefore, with albuminous matters; fermentation with starch, sugars and their immediate derivatives.

Some important forms of fermentation are—

1. The Vinous, producing chiefly Alcohol, C_2H_6O, and Carbon Dioxide, CO_2.

2. The Acetous, producing chiefly Acetic Acid, $C_2H_4O_2$.
3. The Lactic, producing chiefly Lactic Acid, $C_3H_6O_3$.
4. The Butyric, producing chiefly Butyric Acid, $C_4H_8O_2$.

Each variety of fermentation is dependent upon and caused by special forms of microörganisms and enzyms. Substances that prevent fermentation are termed *antizymotics*.

PUTREFACTION is a change which substances containing nitrogen undergo when exposed to air. They are usually converted into simpler products, some of which have characteristic and offensive odors, due in part to sulphur and phosphorus. Putrefaction is caused by the development of various forms of microörganisms and by action of enzyms. Substances which prevent this development will prevent the putrefaction, and are called *antiseptics*.

DECAY.—This is the decomposition of organic bodies by the slow action of oxygen. It takes place too slowly for any increase of temperature to be noticed, and it is rarely complete, that is, some portions of the elements escape action. When wood burns with a flame it leaves nothing but the incombustible mineral matter or ash, but when it decays a brown powder is left, which contains some of the original carbon and hydrogen. Decay requires the access of air, the presence of moisture, and a temperature above the freezing point.

(*h*) SUBSTITUTION.—A process by which one or more atoms of a molecule are removed and their place occupied by an equivalent number of atoms of some other element. The atoms replace one another strictly according to valency. Numerous substitution compounds are described further on; it will be sufficient here to outline the general principles of their formation.

1. *Substitution by Oxygen.*—Oxygen substitutes hydrogen, one atom replacing two of hydrogen; at least two atoms of oxygen are required, one to combine with the liberated hydrogen and the other to take its place. Thus alcohol, when exposed to oxidation, gives the following reaction:—

$$\underset{\text{Alcohol}}{C_2H_6O} + O_2 \rightarrow \underset{\text{Acetic acid}}{C_2H_4O_2} + H_2O.$$

The bodies produced by substitution of oxygen are mostly acids.

2. *Substitution by Chlorine.*—Chlorine usually substitutes hydrogen; one atom of chlorine takes the place of one atom of hydrogen, but the hydrogen thus set free combines with an atom of chlorine; so for the complete reaction two atoms of the latter are needed. Thus:—

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl.$$

If further substitution occurs it will be similar:—

$$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl.$$

These reactions are generally obtained by the direct action of chlorine on the organic body. Proceeding in this way with CH_4, it is possible to remove all the hydrogen and form CCl_4. This method of substitution is an important means of forming compounds between carbon and the halogens.

Bromine and iodine follow substantially the same law, but do not act so readily.

By the action of phosphoric chloride, hydroxyl is frequently substituted by chlorine. This is exemplified in the following reaction:—

Acetic acid — Acetyl chloride — Phosphoric oxychloride

$$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl.$$

3. *Substitution by Sulphur.*—Sulphur substitutes oxygen, atom for atom, but only comparatively few of such substitution compounds are as yet known. They are usually of disagreeable odor. An example of a sulphur substitution is C_2H_6S, which corresponds to alcohol, C_2H_6O.

4. *Substitution by* NO_2.—This is a substitution for hydrogen, and is the result of the action of strong nitric acid. Each molecule of NO_2 replaces one atom of H. The bodies thus formed are called nitro-compounds, the prefixes bi-, tri-, etc., being used to indicate the presence of two or more molecules of NO_2. The action of nitric acid on benzene results in the formation of nitrobenzene:—

$$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O.$$

5. *Substitution by* HSO_3.—Many organic bodies, especially those containing only hydrogen and carbon, when treated with sulphuric acid, form substitution compounds, called *sulphonic acids*, in which the molecule, HSO_3, takes the place of hydrogen in the organic body. Benzene, for instance, gives—

Benzenesulphonic acid

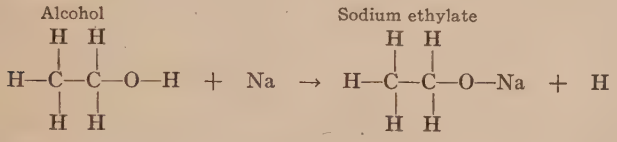
$$C_6H_6 + H_2SO_4 \rightarrow C_6H_5HSO_3 + H_2O.$$

The C_6H_5 replaces the hydroxyl of the acid, not hydrogen alone.

Other Substitutions.—Nitrogen may, under certain circumstances, be substituted for hydrogen.

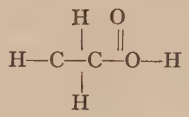
Substitution by Positives.—As positive elements do not unite readily with carbon, they are not likely to substitute hydrogen unless the latter is in

direct union with a negative. Oxygen and sulphur are the only strong negatives that occur in natural organic bodies. When hydrogen is united to either of these, it is easily displaced by such powerful positives as sodium and potassium. They will displace hydrogen when it is in form of hydroxyl, but the less powerful positives, such as zinc, iron and copper, displace hydrogen easily only when it is in a carboxyl group. Positive elements are, therefore, tests for recognition of hydroxyl and carboxly groups. The hydrogen that is joined to the carbon is not replaced in these reactions.

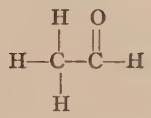


The five hydrogen atoms in association with the carbon are not replaced by sodium.

Zinc will not replace the hydrogen of the hydroxyl of alcohol but with acetic acid a reaction occurs because the acid is ionized, and, therefore, more active. This ionization is due to the fact that the hydrogen in the hydroxyl is united to carbon which is also united to oxygen as the structural formula shows:



In aldehyde—



no hydrogen is easily replaceable by positives, as none is in direct union with oxygen.

Fractional Distillation.—When a liquid contains two or more substances of different boiling points, a partial separation of these may be made by distillation, changing the receiver from time to time. Each liquid distils over at about its boiling point. The most volatile constituent distils first and as each constituent passes off, a thermometer immersed in the vapor shows steadily rising temperature. The separate

portions are termed *fractions*. It is usually not possible to separate compounds completely by this method. The adhesion between liquids and vapors causes some of the material of higher boiling point to be carried over at a lower temperature. Thus, a mixture of common alcohol and water can be distilled so as to reduce the amount of water to about 5% of the distillate, but absolute alcohol cannot be so obtained.

Fractional distillation is largely used in the separation of the hydrocarbons of petroleum and coal tar.

Light and Electricity.—Many organic bodies are affected by light, but the action is usually superficial unless fresh portions are constantly exposed. A mixture of gelatin and potassium dichromate is rendered insoluble by light, and commercial betanaphthol is slowly darkened. Radioactivity also causes changes.

Electricity produces combination and decomposition of organic bodies. Electrolysis can be obtained with many compounds.

Methods of Examining Organic Substances and Elucidating Structure

The *analytic processes* employed in organic chemistry are numerous and often complex. The "ultimate" analysis, that is, determination of the proportion of each element present, is simple in principle but sometimes difficult in practice. To determine the arrangement of the atoms and the exact formula involves many special processes. All that can be given in the present work is an outline of some of the processes of widest application. Among these are determinations of certain data termed **physico-chemical data or constants,** which are of great value in identifying organic bodies, ascertaining purity and elucidating formulas. The following are the more widely applicable methods:

Specific Gravity.—Specific gravities of liquids and solids are generally expressed by comparison with water. Confusion and inconvenience have arisen from the fact that results have been referred to water at different temperatures as unity. The temperatures of observation and comparison should always be expressed. $\frac{100^\circ}{15.5^\circ}$ indicates a determination at 100° and comparison with water at 15.5° as unity. It is best to compare the substance and the standard at the same temperature.

Hydrometers are much used for the determination of the specific gravity of liquids, but the indications are only approximate. Sensitive hydrometers with slender stems, and accurately graduated, are now obtainable.

These are capable of furnishing fair results. Care should be taken to the reading at the top, center or bottom of the meniscus according to the method used in the graduation of the instrument. Instruments intended for use with opaque liquids should be graduated to be read at the top of the meniscus.

Melting and Solidifying Points.—The determination of these is often difficult. Many substances, especially fats, assume conditions exhibiting abnormal melting points, and also frequently solidify at a temperature very different from that at which they melt. If, in the preparation of any substance for determining its melting point, it is necessary to make a previous fusion, the mass should be allowed to rest not less than twenty-four hours after solidification before making the experiment. Chemists disagree as to whether the melting point should be considered to be that at which the substance begins to be liquid or that at which the liquid is perfectly clear. Ordinary thermometers are frequently inaccurate, the error amounting to a degree or more. No observations in which precision is required should be made with unverified instruments.

Boiling Point.—For this determination, the barometric pressure must always be noted and allowance made for the departure from the standard pressure, 760 mm.

Vapor Density.—This is the density of the substance in a state of gas as compared with some standard (generally hydrogen) at the same temperature and pressure. The determination is largely used in organic chemistry, and several methods of procedure have been devised.

Freezing Point of Solution, Cryoscopy.—This method, originally applied for determination of molecular weights, is also used as a clinical test, observations being made especially with urine and blood. The depression of the freezing point of these is regarded as of considerable value in diagnosis. If this clinical application calculations of molecular weight are not made, the data being interpreted by comparison with the average of normal fluids.

Polarimetry.—Polarimeters are instruments used to measure the extent and direction of the rotation of the plane of polarized light. They consist essentially of a Nicol's prism as polarizer, a tube carrying the substance to be tested, and second Nicol's prism or analyzer, by which the extent of rotation is measured. In all forms some condition of the field of vision is fixed upon as the zero point, and the rotation of the analyzer or other manipulation necessary to restore this standard field affords the measurement of the rotation caused by the interposed substance. The form

in common use at present is that known as the "half-shadow" instrument, which uses white light, but gives a field in which the contrasts are without distinct color, merely differences of illumination. These instruments have been brought to a high degree of convenience and accuracy.

Percentage Composition and Determination of Formula.—The composition of any substance may be expressed without use of symbols, or indication of the number of atoms of the elements present. The *parts by weight* of each element contained in 100 *parts* of the substance may be given. The composition of table sugar may be stated as:

Carbon	42.11
Hydrogen	6.43
Oxygen	51.46
	100.00

These figures represent *percentage composition.*

Such methods of expression, though simple and representing facts alone, are not convenient. No satisfactory comparison as to the composition of different compounds can be reached except by the construction of formulas in which the elements are represented by the relative numbers of atoms probably present.

By dividing each figure by the atomic weight of the element, and clearing of fractions, as nearly as can be done conveniently, the number of atoms of each element will be obtained. For example:

$$42.11 \div 12 = 3.51 \times 3.4 = 11.93$$
$$6.43 \div 1 = 6.43 \times 3.4 = 21.8$$
$$51.56 \div 16 = 3.24 \times 3.4 = 11.01$$

The factor 3.4 is used for a multiplier because it is one of the smallest that will give products close to integers.

The last column indicates the formula, $C_{12}H_{22}O_{11}$; that is, this formula, when calculated to percentage composition, will give figures practically identical with those actually obtained by analysis of a sample of cane sugar.

It is evident that any multiple of this formula would also correspond to the percentage composition, hence it is necessary to fix the numbers more rigidly. The lowest term is by no means always the proper formula. The following list exemplifies this. Each formula is correct only for the body indicated; a multiplication or division of it is inaccurate.

		Molecular weight
Formaldehyde	CH_2O	30
Acetic acid	$C_2H_4O_2$	60
Lactic acid	$C_3H_6O_3$	90
Tetrose	$C_4H_8O_4$	120
Arabinose	$C_5H_{10}O_5$	150
Dextrose	$C_6H_{12}O_6$	180
Mannoheptose	$C_7H_{14}O_7$	210

The formula is fixed in each case by the molecular weight. The determination of this becomes, therefore, an important matter. Several methods are in use; among the most frequently employed are determinations of *vapor density, freezing point of solution* and *combining weight.* The procedures for the first two are described in connection with determination of physico-chemical data.

Vapor Density.—This method of ascertaining molecular weight is of wide application and great value. Its use depends upon the fact that when a substance is capable of volatilizing without decomposition, the density of its vapor compared to hydrogen as unity will be *half* the molecular weight.

For example: 1 liter of vapor of common ether is thirty-seven times as heavy as 1 liter of hydrogen gas, the conditions of temperature and pressure being the same. The molecular weight of ether will be, therefore, 74. This corresponds to the formula $C_4H_{10}O$ ($C_4 = 48$; $H_{10} = 10$; $O = 16 = 74$). No multiple of this formula will correspond to the observed vapor-density. The further elucidation of this formula, expressing its rational form $(C_2H_5)_2O$, is attained by other methods.

All the members of the homologous (see p. 118) series of hydrocarbons, beginning with CH_2, have the same percentage composition, their formulas being multiples of the lowest, but the vapor densities steadily increase as shown in the annexed table (CH_2 has not been obtained).

Formula	Density	Molecular weight
C_2H_4	14	28
C_3H_6	21	42
C_4H_8	28	56
C_5H_{10}	35	70

The exact formula of each member of the series can be fixed by a determination of the molecular weight.

Many organic bodies are decomposed by heat, hence their vapor density cannot be obtained.

Freezing Point of Solution.—The general rule is that when different substances are dissolved in amount proportional to their molecular weights in separate portions of the same solvent, the depression of the freezing point is the same. Experiment has shown that if the dissolved substance and the solvent are in the ratio of 1 molecule of the former to 100 molecules of the latter the depression of the freezing point of the solvent will be 0.62°. The method is not widely applicable, being satisfactory only with substances of low chemical activity. Active bodies, such as acids, bases or salts, give abnormal results.

Combining Weight.—If an organicbody forms a definite compound with any element or with any compound, the molecular weight of which is known, such combination can be utilized in determining the molecular weight. For example, silver oxide reacts with acetic acid to form silver acetate and water. Silver acetate has the percentage composition:

Silver	64.6
Carbon	14.4
Hydrogen	1.8
Oxygen	19.2
	100.0

Proceeding as indicated on p. 110, that is, dividing each percentage by the corresponding atomic weight and multiplying these quotients by a number which will bring the figures close to integers (in this case 1.66). the following figures are obtained:

$$64.6 \div 108 = 0.6 \times 1.66 = 0.99$$
$$14.4 \div 12 = 1.2 \times 1.66 = 1.99$$
$$1.8 \div 1 = 1.8 \times 1.66 = 2.98$$
$$19.2 \div 16 = 1.2 \times 1.66 = 1.99$$

The ratio of the numbers in the last column is substantially 1:2:3:2, hence the formula of silver acetate is $AgC_2H_3O_2$. Here, as in the instance explained on p. 111, any multiple of the formula, for example, $Ag_2C_4H_6O_4$, would satisfy the percentage composition. This uncertainty is eliminated by determining the degree of basic power of acetic acid. If it is a monobasic acid silver acetate will have but one atom of silver; if a dibasic acid then the salt will have two atoms of silver. Experiment shows that acetic acid forms but one series of salts, hence silver acetate must be $AgC_2H_3O_2$, and acetic acid $C_2H_4O_2$. The latter formula can be confirmed by a determination of the vapor density.

Several other methods for determining molecular weight are known, but do not need description here. Many organic bodies exist to which no known method is applicable; hence the formula is not definitely assigned. Starch, for example, has a percentage composition corresponding to the ratio $C_6H_{10}O_5$, but the molecular weight cannot be definitely ascertained by any of the methods available. The origin and transformations of starch suggest complex structure; it is probable that $C_{60}H_{100}O_{50}$ is an approximation to its formula. In such cases the formula is often expressed in the lowest terms with a provisional indefinite coefficient, thus $nC_6H_{10}O_5$.

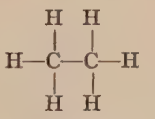
Empirical, Rational and Structural Formulas.—The formulation of organic molecules is based upon the assumption that the valencies of the principal elements are not subject to irregularity. Carbon is always taken as a tetrad, hydrogen as a monad, oxygen as a dyad and nitrogen as either triad or pentad. Phosphorus is usually considered as a pentad; sulphur as either a dyad or hexad. It is, however, freely assumed that polyvalent elements may combine by more than one bond to another atom, even another of the same nature. Thus carbon is assumed to be capable of forming the groups:

$$\equiv C—C\equiv \qquad =C=C= \qquad —C\equiv C—$$

Oxygen is frequently represented as combining by both its bonds, as in the group: H—O—C = O. These double and triple linkings are often termed "unsaturated."

It must not be supposed that a linking by two bonds is a stronger union than by one bond. Valency is a standard of *capacity* of affinity, not of *intensity;* in fact, acetylene which is supposed to contain the triple linking is more easily decomposed than ethane in which the single linking is assumed.

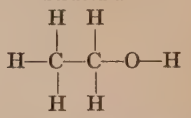
Acetylene



Ethane

Some recent researches have shown the existence of compounds in which carbon is apparently a triad, and others in which oxygen is apparently a tetrad, but the theories in regard to valency are provisional only. For the great majority of organic compounds, the valencies noted above are applicable.

A formula that shows only the number of atoms of each element in the compound is an *empirical* formula; if any supposed arrangement is exhibited the formula is termed *rational*. When the symbols are displayed so as to indicate probable relations of the atoms to each other the formula is termed *structural* (sometimes *graphic*). The following formulas exemplify these terms:

Empirical	Rational	Structural
C_2H_6O	C_2H_5HO	

Some authorities distinguish between *empirical* and *molecular* formulas, applying the former term to the simplest formula that corresponds to the *percentage composition*, and the latter term to formulas that correspond to the *molecular weight*. Under this distinction, CH_2O would be the *empirical* formula of all the bodies in the list on p. 111 and would be the *molecular* formula of *formaldehyde* only. In this work, the terms are used synonymously.

In some substances the atoms are subject to changes of position without altering the identity of the substance. Thus phloroglucol, $C_6H_6O_3$, can be represented by either of the following formulas:

Symmetric trihydroxybenzene	Triketohexamethene
$C_6H_3(HO)_3$	$(CH_2)_3(CO)_3$

Molecules that exhibit this variability are termed *tautomeric* or *desmotropic*.

A *general formula* is an algebraic expression for representing the formulas of a group of bodies, for illustration of which see "Homologous Series."

Ordinary structural fomulas represent the atoms arranged upon the same plane, but as molecules occupy space it is desirable to formulate them on a three-dimensional system. As a basis for this, the carbon atom is represented as a tetrahedron. It is not assumed that this is the shape of the atom, but the four apexes of this solid correspond to the four valencies usually manifested by carbon. Such formulas are termed "*stereochemic*." They can only be saitsfactorily shown by models. Carbon atoms joined by one valency are represented by connecting the models by apexes; atoms joined by two bonds, by connecting the models by edges (see p. 116) and union by three bonds, as is assumed in acetylene, by joining the faces of the tetrahedrons.

Optical Activity. Asymmetric Atoms.—*Optical activity* is the power to rotate polarized light. It is possessed by many bodies, but in organic chemistry is of importance only when exhibited by substances in liquid form, that is, in fusion or solution. The rotation may be either to the right or left. Substances exhibiting rotation to the right are termed dextrorotatory, indicated by + or *d*; substances rotating to the left are termed levo- (lævo) rotatory, indicated by − or *l*.

Asymmetric Atoms.—Any atom that has each of its bonds united to an atom or molecule of different nature is asymmetric. Asymmetric carbon is the most important example. In structural formulas, it will be indicated in this work by an italic symbol. (See, for example, the formula of tartaric acid, p. 146.)

A general relation exists between this position of the carbon atom and the optical activity, expressed by the rule that "every carbon compound that, in the liquid condition, rotates polarized light, will have in its molecule at least one atom of asymmetric carbon." The reverse of the proposition is not true. Asymmetric carbon may be present in substances that do not rotate polarized light. In fact, many substances containing asymmetric carbon exist in three conditions, dextro- and levorotatory, and inactive. The inactive condition may depend upon the antagonistic influence of the asymmetric carbon atoms within the molecule (neutralization by internal compensation) or upon the presence of equivalent quantities of the opposing active substances (neutralization by external compensation).

An acid to which the rational formula $H_2C_4H_4O_6$ is assigned, exists in three forms:

Ordinary tartaric acid.....	Dextrorotatory.
Levotartaric acid.....	Levorotatory.
Mesotartaric acid.....	Inactive. (Not a mixture.)

Racemic acid is often included as a form of tartaric acid, but it is a mixture of equivalent amounts of the *d* and *l* forms. Such associations are occasionally found in nature and the condition has been called "racemism." In mesotartaric acid antagonistic asymmetric carbon atoms are present. The latter condition cannot exist in bodies having but one asymmetric carbon atom in the molecule. (For structural formula of tartaric acid, see p. 146.)

Isomerism, Metamerism and Polymerism.—The properties of bodies depend not only on the elements present in them, but also on the arrange-

ment of these elements with respect to each other. Different arrangements may be made with the same atoms, and thus substances having the same constitution but not identical will be produced. To all such instances the term *isomeric* is often applied, but it is more satisfactory to limit this term to the instances in which the substances are analogous in structural formula. When the identity is in percentage composition and molecular weight, the structures being of different types, the term *metameric* is applicable. When the identity is in percentage composition, but the molecular weights are multiples, and the structure analogous, the relation is termed *polymeric*. True isomerism is often indicated by the addition of the prefix "iso" to the name of one of the substances. Polymerism is sometimes indicated by the similar addition of "para" to one of the names. The following illustrations will show the application of these principles:

True isomerism

H—C≡N cyanogen. C≡N—H isocyanogen.

Metamerism

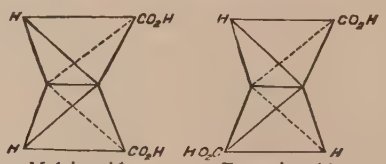
$(CH_3)_2O$ methyl oxide. C_2H_5HO alcohol.

Polymerism

C_2H_4O aldehyde. $C_6H_{12}O_3$ paraldehyde.

In the second instance (metamerism) the formulas merely agree in the total of each atom; no analogy of structure exists.

Instances of isomerism dependent on slight differences in the spatial relations of the constituent atoms are frequently observed in complex molecules. These can only be shown by stereochemic formulas. The term "*allo-isomerism*" proposed for this phase, has not been generally adopted, the usual designation is "stereochemic isomerism." The distinctive nomenclature of these isomers is incomplete. The annexed figures show stereoisomers in each of which two carbon atoms are united by two bonds, indicated by joining the tetrahedrons by the edges.



Maleic acid
Plane symmetric
(or cis-) form

Fumaric acid
Axial symmetric
(or trans-) form

The syllables "cis" and "trans" are used because, in one case, the similar radicals are on the same side of the carbon chain, in the other case on opposite sides.

Organic Radicals.—Any unsaturated molecule may be considered a radical, and hence the number of radicals in the formula of any body will be limited only by the number of divisions that may be assumed, but many groupings that may be imagined, having no coherence or independent function, are not regarded. Any grouping that confers characteristic properties or reactions upon the molecule or that remains unchanged through a series of reactions, is a true radical. Some of these are of frequent occurrence, are always distinguished in rational formulas and often indicated in the name of the compound. The following are examples:

HO, *Hydroxyl.*—The hydrogen of this is easily replaceable by positive elements such as potassium and sodium. When subjected to the action of certain chlorine compounds the entire group is replaced, not the hydrogen alone, as occurs when hydrogen is united to carbon. The presence of one or more hydroxyl groups in a compound is often indicated by the termination "ol," *e. g.*, phenol, C_6H_5HO.

HOCO, *Carboxyl.*—This confers acid properties upon the molecule containing it, that is, such compounds ionize (see p. 16). The *basic* (see p. 24) capacity is proportional to the number of such groups present. Thus acetic acid has but one carboxyl group and is monobasic; tartaric acid has two and is dibasic; citric acid has three and is tribasic.

HCO, *Aldehyde Group.*—The hydrogen is joined to the carbon atom, and is not replaceable by positives. Compounds containing this group often show high reducing power.

$\overset{O}{\underset{CCC}{}}$, *Ketonic Group.*—Carbon united to oxygen by two bonds and by its remaining bonds to carbon atoms that are *not* united to a negative body. This group often confers reducing power on the molecule containing it.

The foregoing groups, it will be noted, do not contain asymmetric carbon and, therefore, do not of themselves produce optical activity.

NH_2, *Amidogen.*—This generally confers capacity for combining with acids, often proportional to the number of groups present. It is indicated by the syllables "amine" or "amide."

NH, *Imidogen.*—This resembles in function amidogen. It is indicated by the syllables "imine" or "imide."

Homologous Series.—Any series of compounds in which the formulas differ by CH_2 or some multiple of this difference by a whole number, is termed a *homologous series*, and the members thereof are *homologues*. These terms are not limited to hydrocarbons. The following are examples of homologous series:

Paraffins	Alcohols	Esters
CH_4	CH_3HO	$(CH_3)_2SO_4$
C_2H_6	C_2H_5HO	$(C_2H_5)_2SO_4$
C_3H_8	C_3H_7HO	$(C_3H_7)_2SO_4$
C_4H_{10}	C_4H_9HO	$(C_4H_9)_2SO_4$

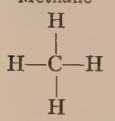
In the third column the constant difference is $(CH_2)_2$, but the series is still homologous. A series intermediate between each member is known, but even if these latter were non-existent, the homology would not be lost.

General Formulas.—The existence of homologous series, renders it possible to express by one formula the molecule of any member of the group. Thus, in the first series, H atoms are always two more than twice the carbon atoms. The general formula, C_nH_{2n+2}, in which n represents any number of atoms, will stand for any member of this series. If it be required, for instance, to write the formula of the sixth member the rule is simple. As the carbon increases regularly one atom at a time, the sixth member will have C_6, that is, $n = 6$. The hydrogen is, therefore $(2 \times 6) + 2 = 14$. The formula is C_6H_{14}. The general formula of the second series above given is $C_nH_{2n+1}HO$; of the third series $(C_nH_{2n+1})_2SO_4$.

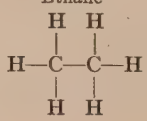
These formulas are sometimes used instead of the series-names. Thus the series beginning with CH_4 is often designated as the series C_nH_{2n+2}.

Carbon Chains.—The valency of each member of a homologous series is the same. The explanation of this is the supposition that, in forming the molecules the carbon has in part satisfied itself, so that each atom of carbon added carries into the molecule only two degrees of valency, which H_2 satisfies. Structural formulas will exemplify this supposition.

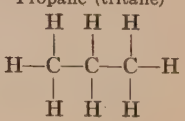
Methane



Ethane



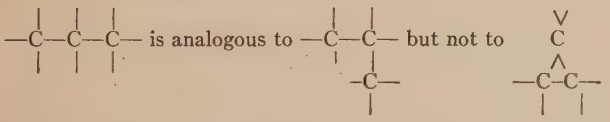
Propane (tritane)



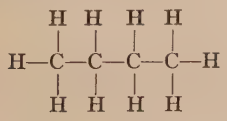
These linked carbon atoms have been called, somewhat fancifully, perhaps, "carbon skeletons." The forms shown above are termed "*open chains*." In other cases the carbon is arranged in a ring of three or more atoms forming "*closed chains*."

Properties of Bodies in the Homologous Series.—The relation of homologous bodies is not a mere accidental relation in formulas. By comparing different members of the same series analogies either in origin, general properties or chemical relations appear. The series beginning with CH_4 is characterized by general indifference to chemical action. The hydroxides of the series beginning with CH_3HO constitute a series of alcohols which possesses specific physiologic action In each series fusing and boiling points, specific gravity and other constants vary with considerable regularity. The molecular weight, of course, increases regularly.

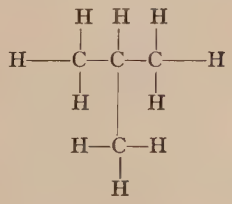
Isomeric Modification in Homologous Series.—Many organic bodies occur in two or more forms not sufficiently distinct to consider them as essentially different, and yet not identical. In such cases, the diagrammatic method of showing the linking of the carbon atoms may be utilized to show that the difference may be due to different positions of the carbon atoms, with respect to each other and to the other elements present. When the number of carbon atoms is less than four, fundamental variation of the carbon chain is not possible, except by closing it, as shown below:



With four carbon atoms two forms may be obtained, as exemplified in the hydrocarbon, C_4H_{10}:



Normal butane.



Isobutane (methyl propane).

The number of possible variations increases rapidly with the number of carbon atoms, so that the higher members of the series show numerous instances. The structural formulas given above may be condensed as follows:

Normal butane.	Isobutane.
$CH_3CH_2CH_2CH_3$	$CH_3CH(CH_3)CH_3$

Classification and Nomenclature of Organic Compounds

Many organic substances are structurally analogous to inorganic substances, and may be classified and named on the same systems as used in inorganic chemistry. The groups termed acids, alkalies and salts, are well represented in organic chemistry. Oxides, sulphides, and halogen compounds are also abundant. Examples of isomerism, polymerism, tautomerism and homology are more numerous in organic chemistry than in inorganic, and hence the methods of classification and nomenclature in the former must be much more elaborate. Unfortunately the systems of naming and arranging organic compounds are still incomplete and unsatisfactory.

In classifying organic substances it is most convenient to begin with the binary forms—the hydrocarbons. These are very numerous and cannot be named according to their formulas, as is so easily done with binary inorganic compounds. Each hydrocarbon has a name referring to some property, source, use or other incidental, often fanciful, relation.

Thus, methane, CH_4, the fundamental hydrocarbon of organic chemistry, because the simplest in structure, was first called *marsh gas*, because it was detected in the emanation from the mud of marshes. The name, methane, is due to the relation of the hydrocarbon to methyl alcohol and this is really a misnomer, for it is derived from a Greek word meaning "wine," to which methyl alcohol has no direct relation. Similarly, the hydrocarbon butane is so named from its structural relations to butyric acid, which is obtained from butter. "Butyric" is derived from the Greek word for butter.

Suggestions have been made to name compounds by syllable systems, according to which the elements should be indicated by their symbols and the number of atoms in each by the vowels in the usual alphabetic order *i. e.*, a = 1; e = 2. By this system CH_4 would be "Caho." These methods have not received serious attention, as they produce jargon.

Nomenclature in organic chemistry is in the main based on the principle that the name shall show the molecular structure or immediate relations

of the substances. It is not usual to base it on properties, but two well-marked instances of this are to be noted. Nitrogenous organic substances termed "enzyms" or "non-organized ferments" are generally distinguished by the termination "ase." Nitrogenous bases are distinguished by the termination "ine." Many substances are as yet not definitely classifiable. For these the termination "in" is provisionally used.

The following is a summary of the principal groups of organic substances:

Hydrocarbons.
Ethers, Alcohols, Aldehyds, Ketones, Esters.
Oils and Fats.
Acids and Salts.
Carbohydrates.
Cyanogen and derivatives.
Amine and derivatives.
Alkaloids.
Azo-, Diazo- and Hydrazo-compounds.
Proteins.
Enzyms.

The distinctions between the groups are not well defined; many substances may be included in more than one group, their molecules exhibiting mixed structure. Thus lactic acid has alcoholic as well as acidic structure. Dextrose which is classed among the carbohydrates has alcoholic and aldehydic structure.

Organic compounds are sometimes divided into two groups termed respectively:

(1) Open-chain or aliphatic compounds, and (2) closed-chain or cylic compounds. This division is also imperfect, in that many substances cannot be assigned positively to either group.

Organic compounds that show analogy to inorganic compounds may be designated by analogous terms. Thus, the formula of common alcohol may be written C_2H_5OH showing a structural analogy to KOH. C_2H_5 is ethyl, alcohol is, therefore, ethyl hydroxide.

To assist in distinguishing organic substances, many syllables have been applied as prefixes or suffixes. A few examples of the more important will be here given. Other less important ones will be mentioned in connection with the compounds that exemplify the use.

"Ane" "ene," "ine," "one," etc., are used for different series of hydrocarbons. The system may be extended by using other vowels and diph-

thongs. In these syllables the penultimate vowel is long. Care must be taken not to confuse these terminations with others apparently similar, namely "one" used to indicate a special form of oxygen compound, called a ketone and the use of "ine" as a termination for basic substances.

"ase" indicates an enzym;

"ose" indicates a carbohydrate, but is also applied to some intermediate products of protein hydrolysis;

"ol" indicates hydroxyl;

"yl" indicates a radical, generally one of uneven valency;

"in" has no exact significance; it is employed largely for bodies not definitely classifiable. It is used for some common enzyms but it would be best to use the proper termination for these;

"al" indicates an aldehyde;

"mono," "di," "tri," etc., are used with analogous significances to those in inorganic chemistry;

"nitro" "chloro" "bromo" "iodo" refer respectively to the presence of NO_2, Cl, Br, I;

"nitroso" indicates the group NO;

"azo" and "diazo" indicate the group $-N=N-$;

"hydrazo" indicates the group $=N-N=$;

"amine" or "amide" indicates the group NH_2;

"imine" or "imide" indicates the group NH;

"thio" indicates sulphur;

"sulpho" is often used instead of "thio";

"pyro" is used to indicate a body that has been obtained by heat;

"sulphonic" indicates the group HSO_3; a salt of this, by replacement of H, is a "sulphonate."

ALIPHATIC OR OPEN-CHAIN HYDROCARBONS

Compounds of carbon and hydrogen are very numerous. Carbon being a tetrad, thegreatest number of atoms of hydrogen that can combine with one of carbon is four. This ompound CH_4, commonly known as *methane*, is the type of the aliphatic or open-chain hydrocarbons; all other compounds of this class are capable of being regarded as derived therefrom by subtraction or substitution, or both.

Substituting all or part of the hydrogen in CH_4 by any other element or group of elements, does not disturb the saturation; the molecule remains a saturated hydrocarbon. Hence the compounds CCl_4, $CHCl_3$, CH_2Cl_2 CH_3Cl will all be referable to the same group as CH_4.

By successive subtractions of H from CH_4, are obtained a series of unsaturated molecules, known as radicals, the valency of which will be, in each case, equal to the number of hydrogen atoms removed. CH_3 is a monad radical because it lacks one atom of hydrogen; CH_2 is a dyad, CHa triad, while C, of course, is a tetrad. From each of these molecules—termed hydrocarbon radicals—derivatives may be obtained, comparable in the main to similar derivatives from the elements themselves. Thus CH_3 forms a chloride, bromide, hydroxide, sulphate, each analogous in formula to the similar compound formed by the elements of the potassium group. CH_2 yields compounds analogous in formulas to those from dyad metals, and so on. In addition these radicals have substitution power, that is, they may replace the hydrogen of other organic compounds. Each of them and each of their derivatives is the first member of a homologous series. A system of nomenclature by terminations has been adopted to distinguish the different series; the vowels are used in regular order, and the syllable *yl* indicates uneven valency. The number of carbon atoms is indicated, except in the first two members of each series, by syllables formed from Greek numerals.

The following table will be sufficient to show the principle of the above classification:

Series 1	Series 2	Series 3	Series 4	Series 5
Gen. formula C_nH_{2n+2}	Gen. formula C_nH_{2n+1}	Gen. formula C_nH_{2n}	Gen. formula C_nH_{2n-1}	Gen. formula C_nH_{2n-2}
PARAFFINS	ALKYLS MONATOMIC ALCOHOL RADICALS	OLEFINS	METHYLENES	ACETYLENES
Methane	Methyl	Methene	Methenyl	Methine
CH_4	CH_3	CH_2	CH	C
Ethane	Ethyl	Ethene	Ethenyl	Acetylene (Ethine)
C_2H_6	C_2H_5	C_2H_4	C_2H_3	C_2H_2
Propane (Tritane)	Propyl (Trityl)	Propene (Tritene)	Propenyl (Tritenyl)	Allylene (Propine)
C_3H_8	C_3H_7	C_3H_6	C_3H_5	C_3H_4
Butane (Tetrane)	Butyl (Tetryl)	Butene (Tetrene)	Tetrenyl	(Crotonylene) Butine
C_4H_{10}	C_4H_9	C_4H_8	C_4H_7	C_4H_6
Pentane	Amyl (Pentyl)	Pentene	Pentenyl	(Valerylene) Pentine
C_5H_{12}	C_5H_{11}	C_5H_{10}	C_5H_9	C_5H_8
Hexane	Hexyl	Hexene	Hexenyl	Hexine
C_6H_{14}	C_6H_{13}	C_6H_{12}	C_6H_{11}	C_6H_{10}

All of these substances have not been obtained, but most of them are known and the others could doubtless be prepared. The members of each vertical column are homologous.

The members of the first series being saturated hydrocarbons, are practically indifferent to chemical reagents. Common paraffin consists of several of them, and the series has therefore been called the "*paraffin series;*" those of the second series, because their compounds are on the type of alkali-metals, are termed "alkyls;" the members of the third series have been called *olefins*, from the older name of one of the members of it.

PARAFFIN OR METHANE SERIES

The members of this series are saturated molecules not easily affected by chemical agents. Many of them are found in petroleum.

Methane, Marsh Gas, CH_4.—This is a colorless and odorless gas which is formed at the bottom of marshes and stagnant pools (whence the name *marsh gas*) as the result of the slow hydrolysis of cellulose.

This decomposition is probably due to the presence of microörganisms. The gas may be collected by filling a bottle completely with water,

inserting a funnel and stirring the decaying vegetable matter in the bottom of the pool while holding the bottle and funnel in an inverted position under the surface of the water. The bubbles which arise may be guided through the funnel into the bottle in order to displace the water.

Methane is a product of ordinary putrefaction and also results from the slow decomposition of certain varieties of coal. When mixed with air it constitutes *firedamp* that causes explosions in coal mines. Coal-gas manufactured for illuminating purposes consists of nearly 50% of methane; the natural gas,largely used for fuel and illuminating purposes in some parts of the United States, is almost pure *methane* (about 90%. In the southwestern United States natural gas containing helium is found.

Ethane, C_2H_6, is a colorless and odorless gas, found in natural gas in small amount s and also existing in crude petroleum.

Propane, C_3H_8; *Butane*, C_4H_{10}; *Pentane*, C_5H_{15}; *Hexane*, C_6H_{14} and *Heptane*, C_7H_{16} are all found in crude petroleum.

Pentane is used as an anesthetic and solvent. The flame of pentane vapor is used as a standard in determining the illuminating power of gas and electric lamps.

Gasolin, now so largely used as motor fuel, is a mixture of the members of the series ranging from about 5 to 8 carbon atoms.

The hydrocarbons or petroleum products boiling between 70° and 120° and having a specific gravity between 0.685 and 0.690 are known under the name of "Ligroin." The use of the terms benzine, benzin and benzolene has led to great confusion between the petroleum products and benzene, C_6H_6, (often called benzol), an important constituent of coal-tar.

Heptane exists in petroleum spirit and also constitutes the greater portion of the oil from *Pinus Sabiniana*.

Kerosene, or *Coal Oil*, is that mixture of the hydrocarbons which is most suitable for burning in lamps.

The hydrocarbons from $C_{16}H_{34}$ to $C_{30}H_{42}$ constitute the various grades of (official) *petrolatum*. Some members of the olefin series are also associated with the paraffins in these compounds. Commercial products not differing materially from petrolatum are sold under trade names.

A mixture of hydrocarbons having a fairly high melting point constitutes the product known as *paraffin*.

Synopsis of the Paraffin Series.—The lowest members of the series at ordinary temperatures are gaseous, the intermediate members liquid and the higher members solid. The boiling points rise with the molecular

weights and in the higher members of the series the specific gravities and melting points show a regular increase.

Derivatives of the Paraffins.—Paraffins are not easily acted upon by chemical agents, but substitution compounds may be obtained by direct action of chlorine and bromine upon all of them, and nitrocompounds may also be produced directly from some of the higher members.

By successive substitution of the hydrogen in CH_4, four derivatives are obtained which will serve as an illustration of the nomenclature of this class of compounds.

Methane	CH_4
Monochlormethane (methyl chloride)	CH_3Cl
Dichlormethane (methene chloride)	CH_2Cl_2
Trichlormethane (methenyl chloride)	$CHCl$
Tetrachlormethane (carbon tetrachloride)	CCl_4

The third substitution, *trichlormethane*, is the important body, *chloroform*, $CHCl_3$. It may be made by the direct action of chlorine upon methane but it is usually made by the action of chlorinated lime upon alcohol or acetone.

When pure it is a colorless, fragrant, mobile, volatile liquid, sp. gr. 1.49, boiling point 60°, sparingly soluble in water, soluble in all proportions in alcohol, ether, petroleum spirit and fixed and volatile oils. It is not readily inflammable, but vapor from boiling chloroform burns with a greenish flame. It is used in analytical chemistry as a solvent. It has marked antiseptic powers. When inhaled it produces deep anesthesia; when swallowed it acts as an irritant. Pure chloroform is unstable; the commercial article contains about 1% of alcohol which acts as a preservative.

Carbon tetrachloride CCl_4, is the final result of the successive substitution of the hydrogen of methane by chlorine. It is a colorless liquid having an odor resembling chloroform; sp. gr. 1.56. It boils at 68°. It is most largely used at the present time as a non-inflammable solvent in manufacturing and technical operations. It is sold for household purposes under the trade name "carbona."

Bromoform, $CHBr_3$, is analogous in composition to chloroform.

Iodoform, CHI_3, is also analogous to chloroform, and is largely used as an antiseptic in surgery. It cannot be obtained by direct substitution of iodine in the methane group, but it is made by the action of iodine on alcohol or acetone in the presence of an alkali. It has a penetrating, dis-

agreeable odor. It crystallizes in bright yellow hexagons, and is soluble in chloroform and ether.

Alkyls, Monatomic Alcohol Radical Series.—This is a series of monad radicals sometimes called the *methyl* series, often the alcohol radicals, because their hydroxides are the common alcohols. The term alkyls is most convenient. The following derivatives are obtained from this series:

Normal oxides called Ethers:

$(CH_3)_2O$, methyl ether, analogous to Na_2O, sodium oxide.

$(C_2H_5)_2O$, ethyl ether.

Compounds with halogens, also sometimes called Ethers:

CH_3Cl, methyl chloride, analogous to NaCl, sodium chloride.

$C_5H_{11}Cl$, amyl chloride.

Compounds derived from acids called Esters or Compound Ethers:

$C_2H_5NO_2$, ethyl nitrite, analogous to $NaNO_2$, sodium nitrite.

$C_5H_{11}C_2H_3O_2$, amyl acetate, analogous to $NaC_2H_3O_2$, sodium acetate.

The compounds analogous to the acid salts are sometimes called Vinic Acids:

$C_2H_5HSO_4$, sulphethylic or sulphovinic or ethylsulphuric acid, analogous to $KHSO_4$.

Hydroxides called Alcohols:

CH_3OH, methyl alcohol, analogous to KOH, potassium hydroxide.

C_2H_5OH, ethyl alcohol.

Compounds containing two different radicals are called Mixed Ethers:

$(CH_3)(C_2H_5)O$, methylethyl ether.

Each compound here mentioned is a member of a homologous series.

In general, when alcohols are oxidized by a limited amount of oxygen, two atoms of hydrogen are removed and no oxygen is added. When oxidized in a free supply of oxygen, an atom of oxygen takes the place of the removed hydrogen. In this way is obtained:

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + O \rightarrow \underset{\text{Ethyl aldehyde}}{C_2H_4O} + H_2O$$

$$C_2H_5OH + O_2 \rightarrow \underset{\text{Acetic acid}}{C_2H_4O_2} + H_2O$$

Thus each alcohol or hydroxide may be made to yield an *aldehyde* (*al*cohol *dehyd*rogenatum) and an acid, each of these being one of a homologous series.

The series of acids is very important; many of them are obtained from fats and oils, hence have been called fatty acids. The following table

Radicals	Oxide, ethers	Hydroxides, alcohols	Aldehydes	Acids	Radical
CH_3 Methyl.	$(CH_3)_2O$ Methyl ether.	CH_3HO Methyl alcohol.	CH_2O Methyl aldehyde. Formaldehyde.	$HCOOH$ Formic acid.	CH_3COOCH_3 Methyl acetate.
C_2H_5 Ethyl.	$(C_2H_5)_2O$ Ethyl ether.	C_2H_5HO Ethyl alcohol.	C_2H_4O Ethyl aldehyde. Acetaldehyde.	CH_3COOH Acetic acid.	$C_2H_5NO_2$ Ethyl nitrite.
C_3H_7 Propyl.	$(C_3H_7)_2O$ Propyl ether.	C_3H_7HO Propyl alcohol.	C_3H_6O Propyl aldehyde.	C_2H_5COOH Propionic acid.	$(C_3H_7)_2SO_4$ Propyl sulphate.
C_4H_9 Butyl.	$(C_4H_9)_2O$ Butyl ether.	C_4H_9HO Butyl alcohol.	C_4H_8O Butyl aldehyde.	C_3H_7COOH Butyric acid.	$C_4H_9NO_3$ Butyl nitrate.
C_5H_{11} Amyl.	$(C_5H_{11})_2O$ Amyl ether.	$C_5H_{11}HO$ Amyl alcohol.	$C_5H_{10}O$ Amyl aldehyde.	C_4H_9COOH Valeric acid.	$C_5H_{11}NO_2$ Amyl nitrite.

gives an outline of some of the important derivatives of this series. One atom of the hydrogen in the acid is replaceable by any positive element or radical, so that it is generally written apart from the other atoms as in $HC_2H_3O_2$ *acetic acid*. In this table only a few of the esters are given.

Isomeric modifications are possible in these bodies, except with methyl, ethyl and some of their derivatives.

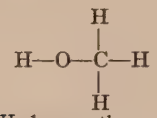
Methods of Forming the Compounds of the Methyl Series.—The starting point is generally the alcohols. The ethers, simple and compound, are produced by the action of acids on the alcohols. The aldehydes are produced by partial oxidation, the acids by complete oxidation; many of the acids exist ready formed in nature.

The alcohols will be described first. They are often called the monatomic alcohols, because they contain a monatomic (*i. e.*, monad) radical.

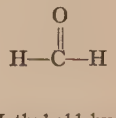
CONSPECTUS OF MONATOMIC ALCOHOLS

Fornula	Systematic name	Common name	Sourse
CH_3OH	Methyl	Wood spirit	Distillation of wood.
C_2H_5OH	Ethyl	Alcohol	Fermentation.
C_3H_7OH	Propyl	Propyl alcohol	"
C_4H_9OH	Butyl	Butyl "	"
$C_5H_{11}OH$	Pentyl	Amyl "	"
		Fusel oil	
$C_6H_{13}OH$	Hexyl	Caproic alcohol	
$C_7H_{15}OH$	Heptyl	Ænanthic "	Action of KOH on castor oil.
$C_8H_{17}OH$	Octyl		From parsnip oil.
$C_9H_{19}OH$	Nonyl		
$C_{10}H_{21}OH$			
$C_{12}H_{25}OH$			
$C_{14}H_{29}OH$			
$C_{16}H_{33}OH$	Hexadecyl	Cetyl "	Spermaceti.
$C_{18}H_{37}OH$			
$C_{30}H_{61}OH$		Triakontyl (myricyl alcohol)	Beeswax.

Methyl alcohol, methanol, wood alcohol, CH_3HO. This was formerly obtained on the large scale only by destructive distillation of wood, but is now made by the interaction of carbon monoxide and water under the influence of a catalyst. The crude product, obtained from wood is mixed with acetone and tarry substances and is offensive in odor, but the pure substance is colorless and with a slight not disagreeable odor. It is highly poisonous and much injury has been done by its substitution, intentionally and unintentionally, for common alcohol. In order to avoid the liability to assume that it has similar uses to common alcohol, chemists are now using only the term "methanol" for it. The crude product is much used for denaturing common alcohol.



Hydroxymethane
(Methanol, carbinol)



Methyl aldehyde
(Formaldehyde)

Formulas showing structural relation between an alcohol and its aldehyde.

Ethyl alcohol $(C_2H_5)HO$, *common alcohol, grain alcohol, spirit of wine, ethanol* is produced in the vinous fermentation of sugar, carbon dioxide being the only other product formed in large amount; it can also be prepared synthetically. The fermented spirit is concentrated by distillation in a rectifying still and column, but the strongest thus prepared contains about 5% of water and constitutes the ordinary alcohol of commerce. *alcohol* To withdraw all water it is necessary to distil with quicklime, anhydrous copper sulphate or calcium chloride, by which *absolute* is formed.

Alcohol is a colorless, transparent, inflammable liquid, of a faint but characteristic odor and a sharp burning taste, sp. gr. about 0.785, boiling point 78°. It is soluble in all proportions in water, ether and glycerol and is largely used as a solvent. *Absolute alcohol* is a slightly better solvent than ordinary alcohol for some volatile oils and resins. It attracts moisture so readily from the air that it is difficult to preserve it in the absolute condition.

Proof-spirit contains, by weight, about 41.5% by weight of absolute alcohol and 58.5% of water and has a sp. gr. of 0.920. *Alcohol* is contained in wine, beer and spirits. Whisky, brandy and other spirits contain from 40 to 50% of alcohol; wines, from 17 (port and madeira) to 7 or

8% (hock and light clarets); porter and strong ale contain from 6 to 8%, lager beer about 3.5%; the mild fermented liquors known as mead, root-beer, spruce-beer, contain from ½ to 1%. The effervescence of fermented liquids is due to the carbon dioxide which is produced with alcohol:

Alcohol

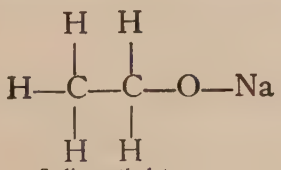
$$C_6H_{12}O_6 \rightarrow 2C_2H_6O + 2CO_2.$$

The carbon dioxide in sparkling alcoholic beverages, is retained by bottling the liquid before the fermentation is over.

In the production of alcohol by fermentation other substances are formed, some of which contaminate the product even after repeated distillation. Among these is *fusel oil* which consists of a mixture of several of the higher members of the same homologous series. The presence of this is indicated by the characteristic odor which is left on filter paper after a small quantity of the alcohol has been allowed to evaporate from it. Aldehyde, which is an oxidation product of alcohol, is often present.

To relieve industrial operations from the burden of the high tax on alcohol, many nations permit addition of offensive substances and on such mixtures, termed "denatured" alcohol, impose no tax or only a trifling one. The principle is that such addition prevents the alcohol being used as a beverage. The substances added depend on the use in which the alcohol is to be employed, thus, alcohol that is to be used for making ether is denatured by addition of ether. Ordinary denatured alcohol contains crude methanol and petroleum products.

Sodium ethylate is obtained by the action of sodium upon alcohol. The substitution takes place rapidly, hydrogen being evolved, but only the hydroxyl group is attacked. The resulting compound is a solid, very soluble in water and alcohol, and corrosive. It saponifies fats more rapidly than an aqueous solution of sodium hydroxide.



Sodium ethylate

Propyl alcohol, propanol C_3H_7OH, exists in two forms. One of these designated as isopropyl alcohol is now a commercial alcohol being made

from natural gas. It has been introduced into the market under the name "petrohol." It can be used as substitute for common alcohol in many ways.

Butyl alcohol, butanol C_4HO_9H, exists in several forms. The normal form is now a commercial article (see below).

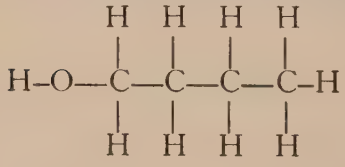
Amyl alcohol, Pentyl alcohol, $C_5H_{11}HO$.—Eight isomers, four primary, three secondary and one tertiary (for explanation of these terms, see below) are possible; all have been obtained. Several of them contain asymmetric carbon. Some of the amyl alcohols are by-products in vinous fermentations and found in alcoholic beverages. They are especially noticeable in the fermented liquor from potato starch (hence the name "amyl" alcohol, from a Greek word for starch). These alcohols may be separated in part by distillation. The mixture of them thus obtained is known commercially as "fusel oil." It was supposed to be very poisonous and to give very injurious properties to liquors containing even small amounts, but these views are now disproved. The pure amyl alcohols are colorless liquids, nearly insoluble in water and of a hot, acrid taste.

The higher alcohols are mostly oily liquids or wax-like solids.

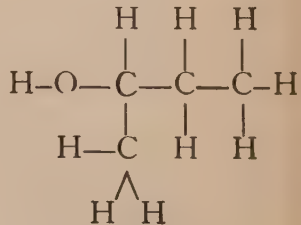
Isomeric Forms of Alcohols.—Methyl and ethyl alcohols present only one form, but a number of isomers of the higher alcohols have been obtained. Comparison of these isomers has led to their division, according to an assumed arrangement of the carbon atoms, into three groups, primary, secondary and tertiary alcohols.

Primary alcohols contain the group CH_2OH joined to *one* alcohol radical; secondary alcohols contain the group CHOH joined to *two* radicals; and tertiary alcohol contains the group COH, joined to *three* radicals.

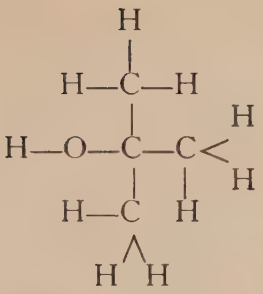
Illustrations of these principles are found in the structural formulas of the three butyl (tetryl) alcohols. The secondary form contains asymmetric carbon indicated by italic symbol:



Primary butyl alcohol



Secondary butyl alcohol



Tertiary butyl alcohol

ETHERS

The primary alcohols, by the action of bodies which have an affinity for water (sulphuric acid, phosphoric acid), are converted into oxides, called *ethers*. A *compound ether* or *ester* is the replacement of the hydrogen of an acid by one or more molecules of a hydrocarbon. The only simple ether of any importance is:

Ethyl oxide $(C_2H_5)_2O$, *Ether*, often wrongly called "sulphuric ether," made by the action of sulphuric acid upon alcohol. Acid ethylsulphate is first formed and then decomposed:

$$\underset{\text{Alcohol}}{(C_2H_5)HO} + H_2SO_4 \rightarrow \underset{\text{Acid ethylsulphate}}{(C_2H_5)HSO_4} + H_2O.$$

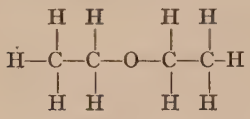
Another molecule of alcohol is then acted upon, thus:

$$(C_2H_5)HO + (C_2H_5)HSO_4 \rightarrow H_2SO_4 + \underset{\text{Ether}}{(C_2H_5)_2O}.$$

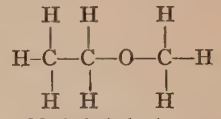
It will be seen from these reactions that in theory the sulphuric acid is continuously re-generated and therefore a small amount of the acid would suffice indefinitely. This is not true in practice on account of reactions between the acid and impurities in the alcohol.

Ether is a colorless mobile, very volatile liquid, of a characteristic odor, boiling at 37°. Sp. gr. 0.723. It is slightly soluble in water, freely in alcohol and is a solvent for fats, fixed and volatile oils, resins and many other proximate principles. The vapor is anesthetic. In using ether it must not be overlooked that while one of the lightest of common liquids, its vapor is one of the heaviest of common gases, and that both liquid and vapor are highly inflammable.

The molecular structure of simple and mixed ethers is illustrated by the annexed formulas:



Ethyl ether



Methylethyl ether

Esters, Compound Ethers.—Many of these have characteristic odors and are the flavoring materials of flowers and fruits.

The usual method of preparation is to heat a mixture of the sodium salt of the proper acid with the alcohol containing the proper radical and sulphuric acid. Thus, to produce ethyl acetate, sodium acetate, ethyl alchol and sulphuric acid are used:

$$C_2H_5HO + NaC_2H_3O_2 + H_2SO_4 \rightarrow \underset{\text{Ethyl acetate}}{C_2H_5C_2H_3O_2} + NaHSO_4 + H_2O$$

Mixtures of esters are used as imitation flavors. The following are the more important.

Methyl acetate, $CH_3C_2H_3O_2$, is a colorless liquid used as a solvent. In association with acetone, it dissolves pyroxylin.

Ethyl acetate, $C_2H_5C_2H_3O_2$, is a colorless liquid of a characteristic agreeable fruity odor. It is largely used in compounding fruit essences.

Ethyl butyrate, $C_2H_5C_4H_7O_2$, is also largely used in artificial flavoring extracts.

Ethyl bromide, C_2H_5Br, is an anesthetic.

Ethyl nitrite, $C_2H_5NO_2$, is the active ingredient of the official spirit of nitrous ether, commonly known as sweet spirit of nitre. (*Spiritus œitheris nitrosi.*)

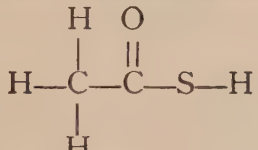
Amyl nitrite, $C_5H_{11}NO_2$, is made by the action of nitric acid upon amyl alcohol. It is a yellowish liquid, of well-marked odor, boiling at 96°. It is used in medicine by inhalation, for the relief of angina pectoris.

Amyl acetate, $C_5H_{11}C_2H_3O_2$, is another of the esters largely used in compounding artificial fruit flavors. It is also used as a solvent, especially in preparing lacquering solutions and the so-called pyroxylin varnishes.

Diethyl phthalate, $C_6H_4\ (COOC_2H_5)_2$, has acquired much importance lately on account of its use in denaturing alcohol. It is a somewhat oily liquid not very soluble in water and of a strong bitter and somewhat numbing taste. It has been used under the presumption that its bitterness would prevent the use as a beverage of any liquid in which was present in small amount (a few per cent). It is comparatively easily detected.

Sulphur Alcohols, Mercaptans.—The oxygen of organic bodies, as of inorganic bodies, may be replaced by any other element of the oxygen group. Ethyl alcohol, for instance, has a corresponding sulphur compound, C_2H_5HS, called mercaptan. This is a condensation of a Latin phrase meaning "to take mercury" on account of its action on that element. The proper name is ethyl hydrosulphide. The mercaptans when oxidized form sulphonic acids which will be taken up later. Corresponding ethers also are known; thus $(C_2H_5)_2S$, ethyl sulphide. These derivatives are mostly strong-smelling and irritating compounds. A few of them exist ready formed in the secretions of animals and plants. The essential oils of mustard, garlic and horseradish are examples, and are noticed elsewhere.

When the oxygen of carboxyl is replaced by sulphur the prefix "thio" or "thi" is generally employed. The following structural formula shows one of the positions of the sulphur atom. These bodies are, as exemplified by those just mentioned, mostly of strong, disagreeable odor.



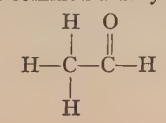
Thiacetic acid

When two atoms of oxygen are replaced the prefix "dithio" is used.

Aldehydes.—These compounds are formed by the removal of two atoms of hydrogen from the corresponding alcohols, and stand intermediate between the alcohols and the acids.

Ethyl aldehyde, ethanal, usually called *acetic aldehyde,* or simply *aldehyde,* C_2H_4O, is often present in liquors, especially in raw forms of commercial spirits. It is a colorless, volatile liquid, lighter than water, and boiling at 21°, having a powerful affinity for oxygen, and therefore a reducing action. It presents several isomeric modifications, one of which, *paraldehyde,* a polymeric form, to which the formula $C_6H_{12}O_3$ has been assigned, has hypnotic properties. All the aldehydes of the series form complicated compounds, as yet of little practical value.

The structural formula of common aldehyde is:



It will be noted that no hydroxyl is present, and hence aldehyde has neither acid nor basic properties.

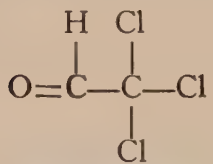
Chloral.—The substitution of three atoms of hydrogen in aldehyde, by chlorine, produces a colorless liquid, trichloraldehyde, C_2HCl_3O, chloral. It combines with one molecule of water to form a crystalline, pungently smelling solid, soluble in water, which is now used under the name of *chloral hydrate*. In alkaline solution chloral is decomposed as shown in the following equation:

Chloral	Sodium hydroxide	Sodium formate	Chloroform

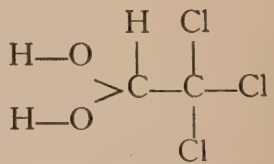
$$C_2HCl_3O + NaHO \rightarrow NaCHO_2 + CHCl_3.$$

Chloral hydrate is really trichlorethene glycol $C_2HCl_3(HO)_2$, derived from ethene glycol $C_2H_4(HO)_2$ (see p. 143) by substitution of Cl_3 for H_3.

Chloral hydrate is hypnotic and sedative and often used for drugging liquor to assist in the commission of robbery or rape. It is decomposed by alkalies in the same manner as chloral.



Trichloraldehyde (chloral)



(So-called) Chloral hydrate

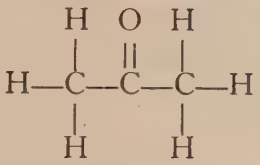
Formaldehyde, CH_2O, has much practical as well as theoretic interest. It is produced by the action of hot copper oxide upon the vapor of methyl alcohol. It is a powerful antiseptic, preserving thoroughly many perishable articles. The use of formaldehyde in preserving articles of food and drink is generally forbidden as it forms insoluble compounds with many proteins and affects the digestibility of the substances thus preserved. It is also a powerful reducing agent. Formaldehyde is considered by plant physiologists as the starting-point in the formation of the so-called "carbohydrates" of the vegetable kingdom. Its formula multiplied by five gives $C_5H_{10}O_5$, pentose, forms of which are common in plants, and by simple changes may produce the sugars and starches. The commercial formaldehyde (formalin) consists of a 40% solution of the gas in water. This solution readily polymerizes with the formation of paraformalde-

hyde, $C_3H_6O_3$, which upon strongly heating again decomposes into formaldehyde.

Ketones.—By the destructive distillation of calcium acetate, a body called *acetone*, C_3H_6O, is formed, differing from aldehyde, C_2H_4O, by CH_2.

$$Ca(CH_3COO)_2 \rightarrow CH_3COCH_3 + CaCO_3$$

Acetone is the type of a group termed *ketones*. They contain carbonyl, CO, united to two monad radicles. They are reducing agents, form "osazones" (see p. 194) and form compounds with sulphites.



Acetone
(Dimethyl ketone)

Acetone is produced in the destructive distillation of wood and is used as a solvent in many technical processes. It is a colorless, transparent liquid, of a characteristic odor, soluble in all proportions in water, alcohol and ether and resembling the latter liquid in its solvent effect on fats, oils and waxes. It is also used as a solvent for pyroxylin.

FATTY ACIDS

This term, applicable strictly to only a few of the series, is applied to the series of homologous bodies derived from the alcohols by substitution of two atoms of hydrogen by one atom of oxygen. These form an extensive and important class; nearly all are natural products. The fixed oils and fats yield some of the higher members of the series. Some have been produced synthetically by a reaction, of which the following is a type:

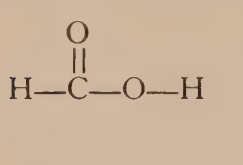
$$\underset{\text{Ethyl alcohol}}{C_2H_6O} + O_2 \rightarrow \underset{\text{Acetic acid}}{C_2H_4O_2} + H_2O.$$

Each of the acids so produced contains one carboxyl group, COOH, the hydrogen of which can be replaced by a positive element or radicle, and this fact may be shown by writing each formula with the carboxyl distinguished. The lower members of the series are freely soluble in, and

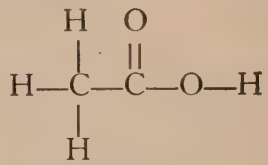
miscible with water, strongly acid and irritating, but as the carbon and hydrogen increase, the compounds become more and more oily. The higher members are feebly acid and insoluble in water, but soluble in alcohol and ether.

Formic Acid, HCOOH, was originally obtained by distilling the liquid in which the bodies of a species of ant (Lat., *formica*) had been macerated. It can be prepared in quantity by heating oxalic acid with glycerol. The glycerol being reproduced, a small amount will suffice for the conversion of much oxalic acid. Formic acid is supposed to exist in the secretions of some stinging animals and plants.

Although formic acid has a higher percentage of oxygen than any other member of its series, it has the greatest reducing power. This is mainly because it contains an aldehydic structure, the group HCO, which is not the case with the other normal fatty acids. The structural formula in comparison with that of acetic acid shows this.



Formic acid



Acetic acid

Formic acid is a colorless, highly irritating liquid.

Acetic Acid, CH_3COOH.—This occurs in small quantities in animal and plant juices. In the dilute form it constitutes vinegar, which contains from 3 to 6% of the acid, and is usually made by oxidizing very weak alcohol in the presence of a ferment. Acetic acid is also produced in the distillation of wood. The first distillate is, in this case, generally contaminated with tar and phenol-compounds and is called pyroligneous acid. It is used commercially in preserving meats. Pure acetic acid is a colorless, corrosive liquid, solidifying at 17° (hence often called "*glacial acetic acid*"), and boiling at 119°. The dilute forms are less active, and in vinegar its effects are quite mild.

Acetates.—The most important of these are:

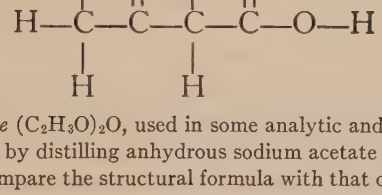
Potassium acetate, $KC_2H_3O_2$, a deliquescent salt, much used in medicine as a diuretic.

Sodium acetate, $NaC_2H_3O_2$, which forms efflorescent crystals, containing $3H_2O$.

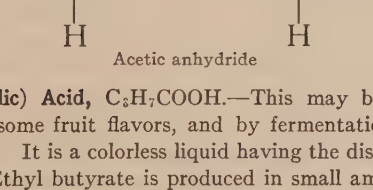
Ammonium acetate $(NH_4)C_2H_3O_2$, is used in medicine in the form of a freshly prepared solution in water, called spirit of Mindererus.

Lead acetate, $Pb(C_2H_3O_2)_2$, *sugar of lead*, made by dissolving lead monoxid in acetic acid, forms white crystals, soluble in water. By boiling this solution with lead monoxid, a considerable amount of the latter is dissolved, and the *subacetate*, more correctly oxyacetate, is formed.

An interesting derivative of acetic acid is *acetoacetic acid*, the structural formula of which is:



Acetic anhydride $(C_2H_3O)_2O$, used in some analytic and research operations, is obtained by distilling anhydrous sodium acetate with phosphoric oxychloride. Compare the structural formula with that of ether (p. 134).



Acetic anhydride

Butyric (Tetrylic) Acid, C_3H_7COOH.—This may be obtained from butter-fat, from some fruit flavors, and by fermentation of sugar with cheese and chalk. It is a colorless liquid having the disagreeable odor of rancid butter. Ethyl butyrate is produced in small amount by heating butter-fat with alcoholic solution of sodium hydroxide. The reaction is not known.

Valeric (Pentylic) Acid, C_4H_9COOH, is found in valerian root and in other plants. Four isomeric modifications are possible. The ordinary form is a colorless liquid of a disagreeable odor. Several valerates, often called valerianates, are used in medicine; among these are those with zinc and ammonium.

Stearic Acid, $HC_{18}H_{35}O_2$, can be obtained from most solid animal fats, and from some vegetable fats. It is a white, crystalline body. It is insoluble in water, slightly soluble in alcohol.

HOMOLOGOUS SERIES OF FATTY ACIDS

Common name	Properties	Natural source
Formic.....	Colorless volatile liquid.	In red ants and some other insects and in some stinging plants.
Acetic.....	Colorless pungent liquid.	Oxidation of alcohol and sugar.
Propionic...	Crystalline solid.	
Butyric.....	Colorless liquid of disagreeable odor.	Butter and other animal secretions.
Valeric.....	Colorless liquid of disagreeable odor.	Valerian root.
Caproic.....	Colorless oily body.	Butter and coconut oil.
Enanthylic..	Slightly soluble in water; has an agreeable odor.	Oxidation of castor oil.
Caprylic....		Butter, coconut and castor oils.
Pelargonic..	Crystalline solid.	Geranium leaves.
Capric.....	Crystalline mass having the odor of sweat.	Butter and coconut oil.
Lauric.....	Silky crystals.	In coconut oil.
Myristic....	Crystalline scales.	In nutmeg and coconut oil.
Palmitic....	Fat-like solid.	Most natural fats.
Margaric....	" "	" " "
Stearic.....	" "	" " "
Arachidic...	White crystalline fatty solid.	Peanut oil.
Behenic.....	" " " "	Oil of ben.
Hyenic.....	Resembles cerotic.	
Cerotic.....	Crystallizes in small grains.	Free in beeswax.
Mellissic....		Derived from beeswax.

Salts of Fatty Acids. Soaps.—By substituting the single atom of replaceable hydrogen of the fatty acids a series of bodies is obtained all of which might be called "soaps," but it is only with the higher members of the series that the peculiar physical and chemical characters of the soaps are noticeable. The derivatives of the lower members are generally soluble in water, but in the higher members most of the compounds are

insoluble, except those formed by potassium, sodium and ammonium. Lead, calcium and zinc, for instance, form insoluble soaps.

The soluble soaps are those which are valuable for their detergent properties. When sodium hydroxide acts on olive oil, a "castile" soap is produced which is hard soap. Potassium hydroxide produces the so-called soft soaps. Among the insoluble soaps which are of common occurrence may be mentioned: Lead plaster which is lead oleo-stearate, made by saponifying olive oil with lead oxide, glycerol being obtained as a by-product. The so-called carron oil, made by adding lime water (solution of calcium hydroxide) to linseed oil, is an insoluble calcium soap formed with the fatty acids of linseed oil.

SUBSTITUTION DERIVATIVES OF THE FATTY ACIDS

The hydrogen that is part of the radical of these acids may be substituted by members of the chlorine group, particularly by chlorine itself. From acetic acid we get three compounds, which resemble the original acid:

$HC_2H_3O_2$ ..... Acetic acid.
$HC_2H_2ClO_2$ ..... Monochloracetic acid.
$HC_2HCl_2O_2$ ..... Dichloracetic acid.
$HC_2Cl_3O_2$ ..... Trichloracetic acid.

These compounds are usually obtained by the direct action of chlorine. By indirect means, the use of phosphoric chloride, PCl_5, for instance, the chlorine may be made to replace the hydroxyl of the acid; in this manner the acid properties are removed, and chlorides formed with the acid radicals. Acetic acid gives the following:

$$\underset{\text{Acetic acid}}{CH_3COOH} + PCl_5 \rightarrow \underset{\text{Acetyl chloride}}{CH_3COCl} + PClO_3 + HCl$$

Similar compounds may be obtained with bromine.

OLEFINS OR METHENE SERIES

Methene, the first member of the series, has not been obtained. *Ethene*, C_2H_4, *ethylene*, the second member of this series, was called, when first discovered, *olefiant* (oil-making) *gas*, because it combines with chlorine to form an oil liquid; for this reason the series has been called the *olefins*. They are dyad radicals, which form alcohols, ethers and other derivatives; but these derivatives are greater in number than from monad radicles,

on account of the higher valency. Two series of acids are yielded by the action of oxygen on the alcohol, instead of one, as in the case of the monad radicals.

The ratio between the weights of the hydrogen and carbon is the same in all hydrocarbons of the series, hence the percentage composition is the same, but the molecular weight increases. The members of the series are, therefore, polymeric isomers.

Derivatives of Olefins.—The olefins combine directly with the halogens. Ethene dichloride $C_2H_4Cl_2$, was originally called *Dutch liquid*, because discovered by an association of Dutch chemists.

By indirect means, oxides, esters and hydroxides may be formed. The hydroxides contain two molecules of HO and are known as Diatomic Alcohols or Glycols. Each of these alcohols yields by oxidation *two* acids, one derived by the replacement of two atoms of hydrogen by one atom of oxygen, and the other by the replacement of four atoms of hydrogen by two atoms of oxygen. The first is the *lactic acid* series; the second, the *oxalic acid* series. For instance, ethene glycol gives the following:

$$C_2H_4(HO)_2 + O_2 \rightarrow H_2O + \underset{\text{Glycolic acid}}{CH_2OHCOOH}$$

$$C_2H_4(HO)_2 + O_4 \rightarrow H_2O + \underset{\text{Oxalic acid}}{COOHCOOH}$$

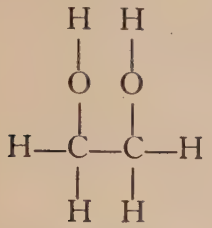
Oxalic acid is, therefore, dicarboxyl. Methene glycol, $CH_2(HO)_2$, has not been obtained. By oxidation it could form but one acid, carbonic, $(HO)_2CO$, which may be regarded as the first member of the first series.

Radical	Oxides, ethers	Hydroxides alcohol	Acids by first oxidation	Acids by second oxidation
			Glycolic acid	Oxalic acid
C_2H_4	C_2H_4O	$C_2H_4(HO)_2$	$C_2H_4O_3$	$C_2H_2O_4$
			Lactic acid	Malonic acid
C_3H_6	C_3H_6O	$C_3H_6(HO)_2$	$C_3H_6O_3$	$C_3H_4O_4$
			Oxybutyric acid	Succinic acid
C_4H_8	C_4H_8O	$C_4H_8(HO)_2$	$C_4H_8O_3$	$C_4H_6O_4$

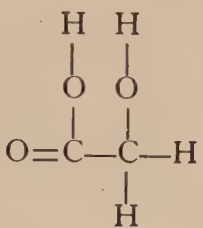
The acids of the first series, containing one molecule of alcoholic hydroxyl and one molecule of carboxyl, are called hydroxy-acids.

Ethene oxide, C_2H_4O, is isomeric (more accurately, metameric) with common aldehyde. It is a three-membered closed chain, the oxygen atom being one member of the chain (see under "Heterocyclic" compounds).

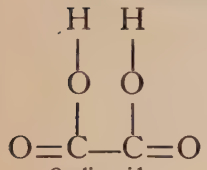
The structural relations of ethene (ethylene) glycol and its two acid derivatives, together with two important salts of oxalic acid, are shown in the annexed formulas:



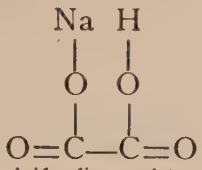
Ethene glycol
(Dihydroxyethane)



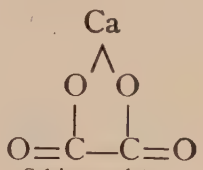
Glycolic acid



Oxalic acid
(Dicarboxyl)



Acid sodium oxalate



Calcium oxalate

Acid Derivatives of the Glycols.—The first (lactic) series is monobasic, that is, has a single atom of replaceable hydrogen; the second (oxalic series) is dibasic, that is, has two atoms of replaceable hydrogen.

LACTIC SERIES

Name	Formula	Source
Glycolic.....	$C_2H_4O_3$	By oxidation of ethene glycol.
Lactic.....	$C_3H_6O_3$	By fermentation of milk sugar.
Oxybutyric....	$C_4H_8O_3$	By oxidation of butyric acid.
Oxyvaleric.....	$C_5H_{10}O_3$	By oxidation of valeric acid.
Leucic.....	$C_6H_{12}O_3$	Occurs in animal products; also formed by decomposition of horn and glue.

Glycolic acid is found in unripe grapes.

Lactic Acid, $(HO)C_2H_4(COOH)$.—This important acid exists in four modifications.

Ordinary lactic acid is a product of fermentation of milk sugar and is therefore found in sour milk and koumyss. It is a colorless, syrupy, very sour liquid, which has not yet been obtained in the solid state. It can be obtained in quantity by allowing a mixture of cane sugar, cheese, sour milk with chalk, or zinc oxide to ferment for several days. The resulting calcium or zinc lactate can be purified and lactic acid obtained from it. It is optically inactive, but consists of equal parts of *d* and *l* forms, which can be separated by several methods. Such separation of isomers is termed "mesotomy" (*Gr.* cutting midway). *d*-lactic acid occurs in the juice of flesh and is sometimes called sarkolactic acid.

Ethene-lactic acid is obtained synthetically by several methods. It is optically inactive.

Several lactates are used in medicine, particularly ferrous lactate and strontium lactate. Lactic acid is one of the products of the growth of fungi around the teeth, and is an important factor in dental caries. When lactic acid is heated in dry air, several anhydrides are formed as follows:

$$2C_3H_6O_3 - H_2O \rightarrow C_6H_{10}O_5, \text{ lactic anhydride}$$
$$C_6H_{10}O_5 - H_2O \rightarrow C_6H_8O_4, \text{ lactide}$$

Lactide is a stable compound.

OXALIC SERIES

Name	Formula	Source
Oxalic.....	$H_2C_2O_4$	Oxidation of sugar, starch, and cellulose.
Malonic.....	$C_3H_4O_4$	Oxidation of malic acid.
Succinic.....	$C_4H_6O_4$	Distillation of amber; oxidation of fatty acids.
Pyrotartaric...	$C_5H_8O_4$	Action of heat on tartaric acid.
Adipic.....	$C_6H_{10}O_4$	" " nitric on sebacic acid.
Pimelic.....	$C_7H_{12}O_4$	" " potassium hydroxide on camphoric acid.
Suberic.....	$C_8H_{14}O_4$	Action of nitric acid on cork or castor oil.
Anchoic.....	$C_9H_{16}O_4$	Action of nitric acid on coconut oil.
Sebacic.....	$C_{10}H_{11}O_4$	Distillation of oleic acid.
Rocellic.....	$C_{17}H_{32}O_4$	Exists in some lichens.

Oxalic Acid, $(COOH)_2$.—The free acid and some of its salts, especially acid potassium oxalate and calcium oxalate, occur in many plants, generally in the form of crystals—called raphides—deposited in special cells. The acid is decomposed by strong heat or the action of dehydrating agents with the production of CO_2, CO and H_2O. When it is heated with glycerol, formic acid is produced.

Oxalic acid forms colorless crystals, having the composition $H_2C_2O_4$, $_2H_2O$. It is freely soluble in water, and poisonous preparations of the acid are sold under the misleading names of *salt of sorrel*, and *salt of lemon*, and used for removing ink stains.

Calcium oxalate, CaC_2O_4, is colorless and insoluble in water. It is a usual urinary sediment occurring in microscopic octohedral or dumbbell crystals. In larger masses it constitutes *mulberry calculus*.

Succinic Acid, $C_2H_4(COOH)_2$.—This occurs in amber and other resins; also in small quantities in some animal secretions. It forms colorless crystals, soluble in water.

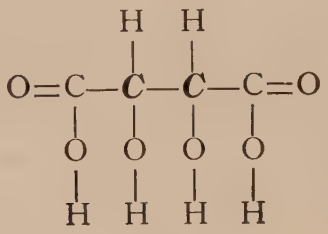
Somewhat related to the series just described, although not necessarily referable to the same radicals, are two important vegetable acids, malic and tartaric. The relation is especially with succinic acid, from which they differ only in amount of oxygen:

	Empirical formulas
Succinic	$C_4H_6O_4$
Malic	$C_4H_6O_5$
Tartaric	$C_4H_6O_6$

Malic Acid, $H_2C_4H_4O_5$, occurs in many tart fruits, as apples and pears. It may be made artificially from succinic acid by replacing an atom of H with OH, or from tartaric acid by reduction and removal of O. It is crystalline, sour, soluble in water and alcohol. The malates are mostly soluble in water.

Tartaric Acid, $(HO)_2C_2H_2(COOH)_2$.—Salts of this acid are found in many plants, especially grapes which contain acid potassium tartrate, $KHC_4H_4O_6$. This is somewhat soluble in water, but less soluble in dilute alcohol; and hence, in the manufacture of wine, as the fermentation advances, the quantity of alcohol increases, and the tartrate deposits as a red mass, called *argol* or *tartar*. When this is dissolved in water and purified by crystallization it constitutes *cream of tartar*. Tartaric acid is obtained from argol by decomposition with sulphuric acid. It is the *d*

form of stereochemic isomers, two of which are, respectively, *d* and *l* and one optically inactive, due to antagonism between the atoms of asymmetric carbon within the molecule. An acid, racemic, (see below) having the same empirical formula and also optically inactive exists, but in this the inactivity is due to mixture of equivalent quantities of the active forms. By inoculating a solution of this acid with common mould (*Penicillium glaucum*) the *d* form is gradually decomposed by the organism, leaving the other form unchanged. This method was discovered by Pasteur to whom the initial investigation in this line is due. There are other methods of mesotomy (see p. 144) for optical isomers.



Tartaric acid

Acid potassium tartrate, cream of tartar, is a white crystalline body, very sour, and not very soluble in cold water. It is used in baking powders because it liberates CO_2 from carbonates.

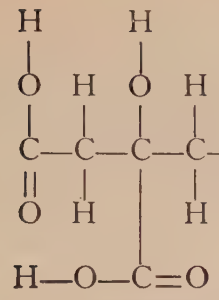
Potassium tartrate, $K_2C_4H_4O_6$, is called soluble tartar.

Sodio-potassium tartrate, $NaKC_4H_4O_6 + 4H_2O$ is known as *Rochelle salt*.

Racemic Acid.—This is the naturally occurring mixture of the two optically active forms. It is found associated with tartaric acid.

Citric Acid, $(HO)C_3H_4(COOH)_3$, is the acid present in lemons, limes and oranges, and some other fruits. It is usually prepared from lemons or limes, which contain from 7 to 10%, but it has also been produced from solutions of cane sugar by the action of certain microscopic fungi. It is normally present in milk. It contains no asymmetric carbon.

It is a crystalline body, very sour and easily soluble in water. It is used in the preparation of effervescing mixtures, but some of the so-called effervescing citrates contain tartaric instead of citric acid.



Citric acid

METHYLENE (METHENYL) SERIES

These are triad radicals. The first member, CH, methenyl, may be regarded as existing in chloroform. The most important member of the group is *tritenyl*, C_3H_5, usually called *propenyl*, also *propylene* and *glyceryl*. Its hydroxid, $C_3H_5(HO)_3$, is glycerol. Many of the common oils and fats are propenyl esters, and when treated with alkalies, such as sodium hydroxide, are broken up a new salt and propenyl hydroxide being formed. On propenyl stearate (one of the ingredients of common animal fat) sodium hydroxide—common lye—would act thus:

Propenyl stearate — Sodium stearate — Glycerol

$$(C_3H_5)(C_{18}H_{35}O_2)_3 + 3NaHO \rightarrow 3NaC_{18}H_{35}O_2 + C_3H_5(HO)_3.$$

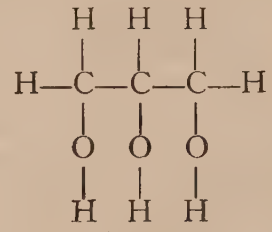
Sodium stearate is a *soap*, and the process is saponification. The formation of glycerol can also be brought about by the use of superheated steam. This method is now generally used, since it gives the fatty-acids in the free condition, thus:

$$C_3H_5(C_{18}H_{35}O_2)_3 + 3H_2O \rightarrow C_3H_5(HO)_3 + 3HC_{18}H_{35}O_2.$$

Glycerol (glycerin), $C_3H_5(HO)_3$.—Pure glycerol is a colorless, viscid liquid, miscible in all proportions with water. Sp. gr., 1.2659. It has a sweet taste, absorbs water from the air, but does not otherwise change. It dissolves a great many substances, standing next to water in its range of solvent powers. It is produced in small quantity during the fermentation of sugar, hence is often found in ordinary liquors. It is sometimes called the "sweet principle of fats," but it does not exist in fats, and possesses no chemical analogy to them. It is an alcohol, and is probably somewhat analogous to the sugars. Its use, therefore, as an appplication

to the skin as a substitute for the emollient oils has no chemical justification, and owing to its strong affinity for water, which it abstracts from the tissues, it often produces irritation when applied in the undiluted state.

When treated with strong nitric acid, it forms propenyl nitrate, $C_3H_5(NO_3)_3$, known as *nitroglycerin*. This is a high explosive. It is now extensively used as a blasting agent, being generally mixed with some inert power such as paper pulp or diatomaceous earth, in which form it constitutes *dynamite*.



Glycerol

FATS AND FIXED OILS

The fats and fixed oils are almost all esters of propenyl. Most of the natural forms are mixtures of two or more distinct esters. Names are applied to them according to the acid from which the ester is derived. (See below.) The fixed oils are fats with a low melting point, and may be divided into two classes; drying oils, which absorb oxygen from the air, and become hard and resinous, such as linseed and poppy oil; non-drying oils, which remain fluid, as castor and sperm oils. Many fats and oils undergo partial decomposition in the air, producing acids, the condition being known as rancidity. When an alkali is added to a fat, decomposition takes place, a salt is formed, constituting a soap, and glycerol is produced. Soaps produced by potassium hydroxide are usually soft; those from sodium hydroxide hard; those made from other oxides are mostly insoluble in water. This latter fact explains the curdling action of limestone waters. The calcium and magnesium compounds in these waters produce insoluble soaps.

The fatty acids may be obtained by adding a strong acid to ordinary soaps.

The fats are all insoluble in water, but are soluble in ether, chloroform, benzene, petroleum spirit and carbon disulphide. They are decomposed

by heat, and consequently cannot, under ordinary circumstances, be distilled.

The proximate constituents of the common fats are given under condensed names, the significance of which is as follows:

Stearin is propenyl stearate.
Palmitin is propenyl palmitate.
Margarin is propenyl margarate.
Butyrin is propenyl butyrate.
Olein is propenyl oleate.

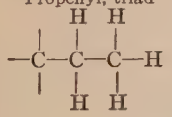
Oleic acid is not a member of the same series with the other acids. It belongs to a series beginning with acrylic acid, $C_3H_4O_2$, and is elsewhere described.

Sterols.—This term includes a group of substances often associated with fats and oils, having a few similar properties such as unctuousness and insolubility in water, but entirely different in chemical character being unsaponifiable and having a hydroxyl group. The most important is *Cholesterol* which occurs in gall-stones and in small amount in blood.

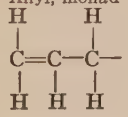
Glycerophosphoric Acids.—Several of these are possible, but the only one of importance is that having the formula $C_3H_5(HO)_2H_2PO_4$. The physiologic relation of this is noted in connection with that of lecithin in the section on Proteins. Some of the complex esters that are found in higher tissues, *e. g.*, brain, nerve-tissue and egg-yolk, are derivatives of this acid. The acid can be prepared by the action of glycerol on orthophosphoric acid.

Allyl and Derivatives.—Allyl, C_3H_5, is isomeric with propenyl, but is a monad, the carbon atoms neutralizing the valency of each other more completely than in the case of propenyl. By structural formulas the difference may be thus represented:

Propenyl, triad



Allyl, monad



Allyl alcohol is C_3H_5HO. It is obtained by the distillation of glycerol in the presence of oxalic acid which acts as a dehydrolyzing and reducing agent. Allyl is interesting on account of the occurrence in nature of two of its compounds, allyl sulphide, $(C_3H_5)_2S$, which is the essential *oil of garlic*, and allyl thiocyanate, C_3H_5CNS, *volatile oil of mustard*. Allyl

aldehyde, C_3H_4O, *acrolein*, is one of the products of the decomposition of fats by head, and is the main mass of the irritating vapors which are caused by such decomposition.

The oxidation of allyl aldehyde gives acrylic acid, which is the first member of a series of acids derived from some of the fats. The most important of this list is oleic acid.

Oleic acid, $C_{17}H_{33}(COOH)$, exists in most natural fats and non-drying oils as olein, propenyl oleate. Above 15° it is a clear liquid, lighter than water, and insoluble in it, but soluble in alcohol and ether. Crude oleic acid, is used in soap making, under the name of *red oil*. Various oleates, *e. g.*, copper, bismuth, zinc and mercury oleates, are now used in medicine to produce the physiological effect of the medicament by local application. They are usually prepared by the reaction of sodium oleate with some suitable compound. Thus, copper oleate is formed by precipitating solution of copper sulphate with solution of sodium oleate.

The derivatives of this series are often termed *unsaturated* compounds because they are capable of taking up negative elements without substitution of hydrogen. The latent valency of a double-linked group, which is in all of them, is developed. Iodine is especially adapted to this action and the proportion of it taken up under specified conditions is known as the "iodine number." It is an important datum in the analytic examination of fatty substances, tar and petroleum products. Some of the fatty bodies containing these unsaturated groups absorb oxygen rather rapidly from the air, becoming viscous. This is commonly termed "drying" and is a property of the oils used in the preparation of paints.

By the action of hydrogen under the influence of a catalyst, a carbon bond can be opened and saturated acid obtained. In this way oleic acid may be converted into stearic.

$$C_{17}H_{33}COOH + H_2 \rightarrow C_{17}H_{35}COOH.$$

By this means a fatty oil can be converted into a solid fat. This method is now largely used. Finely powdered nickel is one of the catalysts used.

ACETYLENE SERIES

This is a series of unsaturated radicals of which the first member, Methine, is C. The second member, Ethine, more commonly known as *acetylene*, has the formula C_2H_2. The structural formula may be expressed thus:

$$\begin{array}{l} C—H \\ \| \\ C—H \end{array}$$

Other members of the series, of less importance, are: Allylene C_3H_4, Butine C_4H_6, Pentine C_5H_8 and Hexine H_6C_{10}. The members of this series are produced in the destructive distillation of many organic compounds. Acetylene is produced by a number of other methods, involving the reduction of methane, ethane, ethylene, etc. It is produced commercially for illuminating purposes by the decomposition of metallic carbides (usually calcium carbide, CaC_2) with water.

$$CaC_2 + 2H_2O \rightarrow Ca(HO)_2 + C_2H_2.$$

The pure substance is a gas. From an ordinary burner it burns with a sooty flame but with specially constructed burners gives flame much brighter than ordinary illuminating gas. It can be liquefied by cold and pressure. The liquid is liable to explode. It dissolves freely in acetone; the solution is stated to be not explosive and used for lighting apparatus for automobiles.

The hydrogen of acetylene can be replaced by strong positives. The compounds formed by members of the potassium and calcium groups are stable, except in presence of water and alcohol, but those of silver and copper are explosive. Although these compounds are *carbides*, yet as they are obtained by reactions with acetylene, an organic body, they are classed as organic compounds. This is, therefore, an instance of the indefiniteness of the term organic.

CARBOHYDRATES

This term was originally applied to sugar, starch and allied bodies, because they contain carbon, hydrogen and oxygen, the latter two in the proportion in which they exist in water, namely, H_2 to O. Two formulas will illustrate this:

Cane sugar	$C_{12}H_{22}O_{11}$
Dextrose	$C_6H_{12}O_8$

This limitation is now known to be inapplicable. Substances strictly analogous to the true carbohydrates, and exhibiting other ratios of hydrogen to oxygen have been discovered. On the other hand, some compounds that exhibit this ratio, acetic acid, $C_2H_4O_2$, for instance, are not included in the group. The term is, however, too well fixed in the nomenclature of chemistry to be displaced at present.

Many substances are included within this group. They are mostly of vegetable origin, soluble in water, optically active and readily susceptible to the action of enzyms and microörganisms, by which they are at first usually hydrolyzed and then split into simpler forms, changes that are exemplified in the common forms of fermentation.

The group of carbohydrates is subdivided as follows:

	Examples
Monosaccharides	Dextrose, arabinose.
Disaccharides	Sucrose, lactose.
Trisaccharides	Raffinose.
Polysaccharides	Starch, cellulose.

The carbohydrates have moderate reducing powers, especially in alkaline solution. Many of them form with phenylhydrazine (see p. 194) characteristic crystalline precipitates called "osazones."

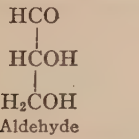
Hydroxyl is a predominating group in the carbohydrates; several molecules are present in even comparatively simple forms. They are, therefore, as a class, alcoholic. They break down through the action of certain fungi, especially yeasts, into simpler bodies which are distinctly

alcoholic, such as ethyl alcohol, some forms of butyl and amyl alcohol, and glycerol. Methanol is not a result of these actions. Many carbohydrates show feebly the properties of acids, but they are not true acids. Several of the sugars, for instance, will form compounds with calcium oxide. A solution of cane sugar will dissolve a notable amount of lime; the compound formed has been termed calcium saccharate or saccharate of lime.

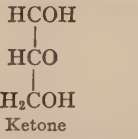
Aldehyde and ketone groups are frequently present in the carbohydrates. The structural formulas of many are known and some have been obtained synthetically. A carbohydrate that contains an aldehydic group is called an *aldose;* a carbohydrate that contains a ketone group is called a *ketose.* A carbohydrate may contain all three of these groupings, and be, therefore, aldehydic, alcoholic and ketonic, a condition that might be condensed into "aldalcoketose" to show the three types and the carbohydrate structure.

MONOSACCHARIDES.—Under this group are included substances containing different numbers of carbon atoms, indicated by the terms monose, diose, triose, etc. Of these the pentoses and hexoses are the most important. Formaldehyde may be considered a monose.

Glycerose, $C_3H_6O_3$, apparently a triose, is actually a mixture of two carbohydrates obtained by the oxidation of glycerol. One of these is an aldose, a glycerol aldehyde, that is, a product obtained by removing H_2 from glycerol without introducing oxygen; the other, a ketose, is the ketone derivative of glycerol. The formulas of these derivatives are, respectively:



Aldehyde



Ketone

Glycerose is of no practical interest, but its application in the synthesis of carbohydrates has given it theoretic importance.

Pentoses exist in many plant tissues and have an important bearing on the nutritive value of vegetable materials, but the details belong to physiology rather than chemistry.

HEXOSES.—Two important hexoses require detailed consideration:

Dextrose, Glucose, Grape Sugar, $C_6H_{12}O_6$.—This exists in many fruit juices and in honey. It is present in small amount in many animal fluids and excretions; in some diseases the amount is greatly increased. In fruit juices and honey it is associated with levulose. Dextrose can be

obtained by the hydrolysis of many carbohydrates by dilute acids or enzyms. Starch, dextrin, cellulose and cane sugar are easily hydrolyzed in this manner.

The principal commercial source of dextrose is by the hydrolysis of starch, usually corn starch, by dilute acid. If the resulting solution is not concentrated beyond the syrupy condition, it will contain maltose, dextrin and several unfermentable carbohydrates not yet clearly isolated in addition to dextrose. If the material is evaporated to solid form, it consists almost entirely of dextrose. The syrupy liquid is commercially called "glucose" and the solid form "grape sugar."

Pure dextrose is a white, crystalline substance, freely soluble in water, to which it imparts moderate sweetness. The solution has strong dextro-rotatory power and is easily fermentable by yeast into carbon dioxide and alcohol. In alkaline solution, it has marked reducing power, liberating copper, lead, silver, gold and platinum from their compounds. It forms with phenylhydrazine an osazone that crystallizes in yellow stellate tufts.

Commercial glucose is largely used as a substitute for other carbohydrates in the fermentation industries, and also as a substitute and adulterant for honey, molasses and maple syrup.

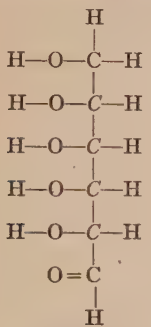
Levulose, $C_6H_{12}O_6$, *d-Fructose*, *Fruit Sugar*.—This is associated with dextrose in fruit juices and in honey, and is produced in equal amount with dextrose in the hydrolysis of sucrose. It can be obtained pure by heating inulin with water at the boiling point for twenty-four hours.

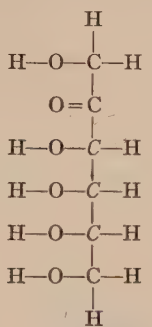
Levulose is soluble in water, forming a sweet liquid that has strongly levorotatory power at ordinary temperatures; less so when hot. It ferments with yeast to carbon dioxide and alcohol, but not so readily as dextrose, hence many fruit-juices, becomes *l*-rotatory when fermented, the dextrose being removed much faster than the levulose.

Notwithstanding the strong *l*-rotatory power of ordinary levulose, it is, on account of its direct structural relations to a *d*-rotatory aldose usually termed *d*-fructose.

Ordinary dextrose and levulose are alcohols, but are not stereo-isomers. The former is an aldehyde, the latter is a ketone. There is, therefore, a form of dextrose having *l*-rotation and one of levulose having *d*-rotation; in fact, theory indicates, and research has confirmed, the existence of numerous isomeric hexoses and derivatives. The annexed formulas show types of the structure of some of these bodies. Asymmetric carbon is present in all. In forming osazones, dextrose and levulose lose the characteristic groupings, that is, dextrose loses the aldehyde group and

levulose loses the ketone group. Hence these hexoses, though not stereoisomers, yield the same osazone.


Hexose with aldehydic structure


Hexose with ketonic structure

By limited oxidation, many carbohydrates yield acids.

Hexose Alcohols.—These contain hydroxyl groups but no aldehydic nor ketonic groups. They resemble the ordinary hexoses in many ways but do not reduce Fehling's solution and are not fermented by yeast. The most important is:

Mannite, Mannitol, $C_6H_{14}O_6$, which is seen not to correspond in its empirical formula to the ordinary definition of a carbohydrate. Mannite exists in three isomeric forms, *d* and *l* and inactive. The *d*-form is a natural product, occurring in several plants, especially in *manna*, an exudation from a species of ash. It may be prepared synthetically by the action of sodium amalgam upon levulose. It is not identical with the substance termed "manna" in the English translation of the Old Testament.

Sorbite, from mountain-ash berries, and *dulcite*, from a Madagascar manna, are similar in composition to mannite. Care must be taken not to mistake the termination in these names for the syllable used in the names of some salts. Sorbitol and dulcitol would be preferable names for these bodies.

Disaccharides.—*Sucrose, Cane sugar*, $C_{12}H_{22}O_{11}$.—This exists in the juices of many plants, but is commercially obtained from few sources: sugar cane, beet-root, maple and sorghum. It is a colorless solid, easily crystallized and very soluble in water. The solution is very sweet and has high dextrorotatory-power. It does not reduce Fehling's solution,

nor form a precipitate with phenylhydrazine. It ferments readily with yeast, but this effect is preceded by a hydrolysis under the influence of an enzym present in the yeast-cell. By this hydrolysis, one molecule of surcose takes up one molecule of water, and divides into one molecule of dextrose and one of levulose. The equation of the reaction is:

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6.$$

The proportions by weight are 95 parts of sucrose to 5 parts of water, yielding 50 parts of dextrose and 50 parts of levulose. As the specific rotatory power of levulose is, at ordinary temperatures, higher than that of dextrose, the resulting mixture is slightly levorotatory, and is termed "*invert sugar.*" The same transformation can be brought about by the action of dilute acids and many mineral salts. It is technically known as an "*inversion.*" The yeast-enzym that inverts sucrose is called "*invertase.*" The fermentation that ensues is produced by other enzyms not yet definitely isolated, and affects the dextrose more actively than the levulose.

Maltose, $C_{12}H_{22}O_{11}$, is produced together with dextrins by the action of common enzyms on starch. It is abundantly present in malt. It is sweet, soluble in water, readily fermentable with yeast, reduces Fehling's solution and forms a characteristic osazone.

Lactose, $C_{12}H_{22}O_{11}$, is the characteristic carbohydrate of cow's milk. Ordinary lactose, obtained from the whey of cow's milk, crystallizes in colorless, gritty masses moderately soluble in cold water and with slight sweetness. The solution ferments readily to lactic acid, but yields alcohol only under the influence of special ferments. In alkaline solution, lactose reduces compounds of silver and copper promptly. It differs from sucrose in not being carbonized by strong sulphuric acid, and in reducing Fehling's solution. It yields a characteristic osazone.

The TRISACCHARIDE, *Raffinose*, is found in association with beet sugar.

POLYSACCHARIDES.—*Cellulose*, $n C_6H_{10}O_5$ is the colorless material of woody fiber. It is seen in cotton or linen in a nearly pure form. It dissolves in an ammoniacal solution of cupric hydroxide but is insoluble in water, ether or alcohol. Strong sulphuric acid converts it either into a soluble substance, like dextrin, or into a substance, giving a blue color with iodin. By long-continued action of dilute sulphuric acid, cellulose is converted into dextrose.

Paper is nearly pure cellulose obtained by boiling vegetable structures with solutions that dissolve the cementing materials. For the best

grades of paper, made from linen and cotton, weak solutions of sodium hydroxide in open vessels are used, but much paper is made from wood, by boiling with strong solutions of sodium hydroxide or magnesium sulphite under pressure. The inferior grades of commercial paper contain much ground wood not chemically treated.

When paper is treated for a short time with a cold mixture of two volumes of sulphuric acid and one of water, it becomes tough and waterproof, and is termed *parchment paper.*

Cellulose may be dissolved and re-precipitated. By mechanical methods the precipitate may be obtained in threads or thin sheets, thus producing artificial textile materials.

Pyroxylin, Gun-cotton.—Cellulose yields with nitric acid a series of nitric esters, having explosive properties. The composition differs with the strength of the acid, temperature and time of immersion. All the products retain the general physical appearance of the original material, but become rapidly combustible, burn with a bright smokeless flame disengage much gas, and leave no appreciable residue. They dissolve, or gelatinize, in liquids which do not affect cellulose. When the degree of nitration is low, the product is soluble in a mixture of alcohol and ether and is called *soluble* or *negative cotton.* The latter term refers to its use in preparing photographic negatives. When the formula contains larger proportions of the nitric acid radicle, the material is highly explosive, less soluble and is known as *gun-cotton.* It is used alone as an explosive and also in the preparation of smokeless powders.

Collodion is formed by dissolving pyroxylin in a mixture of ether and alcohol. This is called *plain collodion.*

Celluloid is prepared from pyroxylin. Flexible celluloid films are now used extensively in photography. Lately, a safer film, prepared by the action of acetic acid, has been introduced.

Glycogen.—This is an animal product, a white, amorphous powder, producing a brown with iodine. By the action of ferments or dilute acids it is converted into dextrose. It, therefore, resembles starch, but is soluble in cold water.

Starch.—This term is applied to a carbohydrate found widely distributed in the vegetable kingdom, in different tissues, but especially seeds, rhizomes and tubers. It is intimately connected with the formation of the cellular structure of vegetables. The conditions of its development have been carefully studied owing to its importance in vegetable physiology. The first step in its formation may be the synthesis of form-

aldehyde under the influence of sunlight in accordance with the following equation:

$$CO_2 + H_2O \rightarrow CH_2O + O_2$$

From the formaldehyde, by polymerization, complex carbohydrates and finally starch may be produced.

The percentage composition of starch corresponds to the empirical formula $C_6H_{10}O_5$; the molecular weight is unknown but is certainly high. The rational formula is also unknown.

Starch is deposited in the cells of plants in minute granules which are sufficiently characteristic in form to permit the source of the starch to be recognized by microscopic examination. In most cases, the granules are spherical or spheroidal. They are often marked by concentric rings and a spot, termed the *hilum*.

Starch is not appreciably soluble in cold water; hot water breaks up the granules, dissolves some of the material and forms with the remainder a jelly of very low diffusive power. The solution has high dextrotatory power. With free iodine, starch produces a deep blue compound, sometimes called starch iodide, but the exact nature of it is not known. It is dissociated by heating the liquid, the mixture becoming colorless, but the color returns on cooling. Solid starch also gives the blue with iodine.

Many enzyms, especially those of malt, saliva, and pancreatic secretion, quickly convert starch jelly by hydrolysis into a mixture of maltose and dextrin. Dilute acids also hydrolyze starch, producing much dextrose with some dextrin.

Inulin is a carbohydrate that exists in the roots of many Compositæ, such as dahlia and chicory. By boiling with water for some time it is completely converted into levulose.

Dextrin.—This term includes several substances. Their composition may be represented by the formula $n C_6H_{10}O_5$. They are produced from starch by direct heating with water and by hydrolysis with dilute acids and many enzyms. They are amorphous, light yellow powders, insoluble in alcohol, soluble in water, forming an adhesive mucilage. The solution is strongly dextrorotatory and does not reduce Fehling's solution. By boiling with dilute acids, the dextrin is converted into dextrose.

The dextrin obtained by heating starch with water under pressure is sometimes called *British gum*. It is used as an adhesive.

Gum Arabic, an exudation from species of *Acacia*, consists chiefly of the calcium and magnesium arabates. It is used in the preparation of mucilage.

Gum Tragacanth.—This is composed of several carbohydrates, some of which are soluble in water and others that do not dissolve, but absorb water in large amount and swell, making an adhesive paste.

Several vegetable gelatinizing materials, such as agar-gar, are probably carbohydrates or closely related to them.

GLUCOSIDES

This term includes a large number of substances, many of vegetable origin. Most of them are easily decomposed into several simpler bodies, one of which is a carbohydrate, usually dextrose. Dilute acids and some enzyms are the usual means of producing these changes, the action being in most cases hydrolysis. A glucoside may, therefore, be regarded as an ester of the carbohydrate yielded by it.

Most glucosides are non-nitrogenous. Many of them are active principles of the plants in which they occur, but in some cases this activity is due to the products of decomposition and not to the glucoside itself. This is the case with mustard, bitter almonds and wild cherry bark. As a rule, the glucosides are associated with the enzym necessary for their decomposition. Starch and some of the other carbohydrates may be regarded as glucosides as they yield dextrose by hydrolysis.

Amygdalin, $C_{20}H_{27}NO_{11}$, exists in the tissues, especially seeds, of many plants of the order Rosaceæ, in association with an enzym called *synaptase.* This acts on the amygdalin, when the seeds are crushed in cold water; but boiling alcohol coagulates the synaptase and dissolves the undecomposed amygdalin. The latter is a white, crystalline body, soluble in alcohol and water, but not in ether. The decomposition to which it is susceptible is explained in connection with the description of hydrogen cyanide.

Salicin, $C_{13}H_{18}O_7$, is found principally in the bark and leaves of the poplar and willow. It crystallizes in white needles; insoluble in ether, but soluble in water and alcohol. Salicin decomposes as follows:

$$C_{13}H_{18}O_7 + H_2O \rightarrow C_7H_8O_2 + C_6H_{12}O_6$$

$C_7H_8O_2$ is called *saligenin.*

Tannins.—These are astringent principles, widely diffused in the vegetable kingdom. They dissolve in water and the solution has an acid reaction; hence they are often called *tannic acids.* Many forms are known; they possess the common property of precipitating gelatin and giving dark-colored precipitates with ferric salts. Their action on gelatin is

utilized in the preparation of leather, and their action with ferric salts in making ink.

Ordinary tannin, gallo-tannic acid, occurs in nutgalls—excrescences formed on a species of oak by puncture by an insect—and sumac. It is usually seen as a loose, brittle, light-yellow, non-crystalline mass, very soluble in water and highly astringent. It gives a bluish-black precipitate with ferric salts. The common form is not entirely a glucoside but contains a large amount of digallic acid, $C_{14}H_{10}O_9$.

When tannin is boiled with dilute acids, or mixed with water and exposed to moist air, it forms a gallic acid by hydrolysis of the glucoside or digallic acid.

Thus:—

Tannin (glucoside) Dextrose Gallic acid

$$C_{27}H_{22}O_{17} + 4H_2O \rightarrow C_6H_{12}O_6 + 3C_7H_6O_5.$$

Digallic acid Gallic acid

$$C_{14}H_{10}O_9 + H_2O \rightarrow 2C_7H_6O_5$$

This process of tanning consists essentially in the tannin rendering the gelatinous matter of the hide insoluble, and therefore not liable to decomposition.

Sinigrin, Potassium Myronate, $KC_{18}H_{10}NS_2O_{10}$.—The seed of the black mustard contains this body and also an enzym, *myrosin,* which decomposes the sinigrin according to the following equation:

$$KC_{10}H_{18}NS_2O_{10} \rightarrow C_3H_5CNS + C_6H_{12}O_6 + KHSO_4.$$

C_3H_5CNS is allyl thiocyanate, to which the irritating action of mustard is due. It will be noted that this is not a hydrolysis.

White mustard seed contains a *sinalbin,* and an enzym, *myrosin.*

Indican, $C_{52}H_{62}O_{34}$, occurs in several plants. By boiling with acids it yields the color known as *indigo blue* (indigotin). Indigo blue is usually obtained from the plants containing indican, by macerating them with water, and exposing to the air until fermentation occurs and blue is deposited.

CYCLIC OR CLOSED-CHAIN HYDROCARBONS

In these compounds, carbon atoms are connected into one or more closed series or chains. Three is the smallest number of atoms that can form such a chain. When the chain is composed of one kind of atoms, it is *homocyclic* or *isocyclic*. This term is generally applied to carbon chains, although obviously not necessarily so limited. The nucleus of three nitrogen atoms in azoimide (see p. 186) is homocyclic. As with the open-chain compounds, some of the valencies may be latent, that is, two atoms may be connected by more than one bond. These latent valencies are developed only under special conditions, giving origin to *additive* compounds.

When the chain includes atoms of different elements, it is termed *heterocyclic*. The more important instances of this arrangement are rings containing two or more carbon atoms linked with an atom of oxygen, sulphur or nitrogen.

These closed-chain compounds may have the same empirical formula as open-chain compounds. The former are, therefore, not infrequently named by attaching the prefix "cyclo" to the name of the open-chain compounds. Thus, trimethene $(CH_2)_3$, isomeric with C_3H_6, propane, is called "cyclopropane."

HOMOCYCLIC COMPOUNDS

Three-membered Rings.—An instance is found in *cyclopropane, trimethylene* or *trimethene*, isomeric with propane.

Four-membered Rings.—The compounds of this type have as yet but little practical interest. Methyl tetramethene, $(CH_2)_3CH(CH_3)$, is an instance.

Five-membered Rings.—A considerable number of derivatives of this type are known. Common camphor yields methene derivatives of this type, but the reactions by which these are produced are not yet known.

Seven-membered rings are also known but they tend to reduce to six-carbon rings.

SIX-CARBON HOMOCYCLIC COMPOUNDS

Three sub-groups of these are distinguished:

Benzenes (aromatic hydrocarbons).
Terpenes (essential oils).
Polynucleated compounds.

BENZENES

Historical Note.—In the manufacture of illuminating-gas by the destructive distillation of bituminous coal and shale and in the manufacture of coke, many products are obtained, some gaseous at ordinary temperatures, others liquid and solid. The liquid and solid bodies are collected in mixture as a dark, thick liquid, with an odor recalling that of the gas. This is known as *coal tar*. For a long while it was a useless by-product and its disposal a serious problem. In 1825 Faraday obtained, by compressing coal gas, a hydrocarbon, which is now known to be identical with that obtained by Mitscherlich in 1834, by distilling calcium benzoate, which, on account of this source, was called "*benzene.*" In 1845 Hofmann discovered the same body in coal tar, and not long afterward, Mansfield, a pupil of Hofmann, prepared it in practicable quantity from the tar. Mansfield lost his life while preparing a sample for public exhibition.

Benzene shows no isomerism in itself, but yields many derivatives among which isomerisms are abundant.

In 1865, Kekulé suggested that its molecule consists of six carbon atoms in a closed chain with six latent valencies and six other valencies satisfied by hydrogen. By this theory, so far, all the numerous derivatives can be formulated consistent with their isomerisms and relations. Moreover, the properties of benzene itself are explained by the theory. Benzene ordinarily exhibits the functions of a saturated hydrocarbon, but, under special conditions, it is capable of forming *additive* compounds, this addition taking place by the simultaneous action of two valencies.

Kekulé's view has been generally accepted, and extended to many other classes of compounds. Some difference of opinion exists as to the manner in which the latent valencies are disposed.

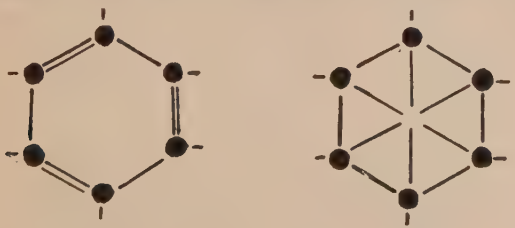
Coal tar contains many substances that are structurally related to benzene; these may be separated, but usually somewhat imperfectly by fractional distillation. It is known that benzene obtained from tar, unless especially purified, contains a compound in which sulphur takes the place

of two carbon atoms. This will be noted under the heterocyclic compounds. Among the important bodies associated with benzene in coal tar, are toluene, phenol, anthracene, naphthalene and pyridin. The benzene occurs in the most volatile portion of the tar, termed light oils. Crude benzene is known in commerce as "benzol," a name which has, unfortunately, been much used for benzene itself.

Benzene, C_6H_6, is a colorless, mobile, volatile liquid with an odor that suggests coal tar. It melts at 5.4° and boils at 80.4°. The solid benzene resembles common paraffin. The sp. gr. of the liquid is 0.899. It has high solvent powers for many substances, notably fats, waxes and resins. It is readily inflammable, burning with a smoky flame, but does not undergo direct oxidation by ordinary oxidizing agents. Benzene forms two classes of derivatives, *additive* and *substitutive*. The former are of little practical interest, but the latter are very numerous and important. Additive compounds of monad elements are formed with even numbers of atoms, *e. g.*, benzene chlorides are $C_6H_6Cl_2$; $C_6H_6Cl_4$; $C_6H_6Cl_6$. The substitution of monad elements or radicals may take place singly, chlorbenzenes, C_6H_5Cl; $C_6H_4Cl_2$; $C_6H_3Cl_3$; $C_6H_2Cl_4$; C_6HCl_5; C_6Cl_6, being known.

It is necessary to distinguish clearly between these two classes of derivatives. The nomenclature used is exemplified above. Additive compounds are named in the same manner as the binary compounds of inorganic chemistry (compare benzene dichloride, $C_6H_6Cl_2$, with zinc dichloride, $ZnCl_2$). Substitution compounds are named by attaching to the fundamental name syllables indicating the nature of the substituting bodies and also numerical syllables; thus, $C_6H_4Cl_2$ is *dichlorbenzene*.

The assumed structure of the molecule of benzene is shown in the following diagrams of the carbon nucleus—the carbon atoms represented by dots—and arrangement of valencies. Two diagrams are given, showing suggestions as to manner and disposition of the latent valencies.



Kekulé Armstrong

Carbon atoms represented by dots.

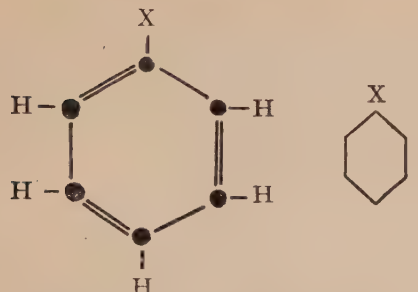
Benzene derivatives obtained by substituting the hydrogen by equivalent atoms or groups are numerous and show many instances of isomerism. These are best explained by tridimensional (stereo-chemic) formulas but such a method is not here available and the ordinary structural formulas must suffice.

The following compounds illustrate these substitutions and the nomenclature of them:

C_6H_5Cl.....chlorbenzene.
$C_6H_4Cl_2$.....dichlorbenzene.
$C_6H_3(HO)_3$.....trihydroxybenzene.
$C_6H_4(COOH)\ (HO)$.....carboxyhydroxybenzene.

For convenience in naming compounds, C_6H_5, is frequently called phenyl, and C_6H_4, phenylene.

The term "hydroxy" in these names is often abbreviated to "oxy." Thus, C_6H_5HO is called oxybenzene. The conditions of symmetry in benzene are such that no isomerism is to be expected (and none has been observed) in the compounds formed by a single substitution of the hydrogen. Hence, phenol (hydroxybenzene)is identical no matter how prepared. When two or more hydrogen atoms are replaced, isomerism at once becomes possible, and very numerous when several different substituting molecules are introduced. To aid in expressing the formulas of these isomeric bodies, and also in distinguishing them by name, the normal benzene molecule is represented by a hexagon which, when unmodified, is read, C_6H_6; it is termed a "ring-symbol." A symbol or formula at any angle of this hexagon indicates that an atom of hydrogen is replaced by the body represented by that symbol or formula. The annexed diagrams will show the detailed structural formula and ring-symbol. The carbon atoms are here again represented by dots. X represents any monad element or monad radical.



Substitution compound and ring symbol
$= C_6H_5X$

The position of the symbol of the substituting body when only one is present is immaterial in this case, but it is usually written at the upper angle. When two hydrogen atoms are replaced three isomeric bodies will be formed, whether the replacement is by the same or different bodies. To assist in indicating these, the angles are distinguished by numbers in the order of those on a clock, thus:

Substitution of two hydrogen-atoms are shown in the annexed ring. symbols.

1–2
ortho

1–3
meta

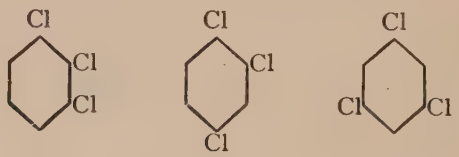
1–4
para

X, as before, represents any monad element or monad radical. It will be seen that 1–5 and 1–6 are identical, respectively, with 1–3 and 1–2, so

that three and only three isomeric forms are to be expected. This accords with all known facts. Moreover, the rule applies to cases in which two different substituting molecules appear. The numerical system is not always used in these instances; the compounds are designated by prefixing the following syllables:

ortho for 1–2
meta for 1–3
para for 1–4

Substitutions of three hydrogen atoms by three atoms or molecules of the same kind give rise to three isomeric forms which are exemplified in the annexed formulas of the three trichlorbenzenes together with distinctions by the two systems of nomenclature in vogue.



1–2–3 Vicinal | 1–2–4 Asymmetric | 1–3–5 Symmetric

If the three substitutions are not of identical substances, the isomerism becomes complex, and substitutions of four still more so. Substitution of five or six hydrogen atoms by identical bodies gives only one form.

No uniform system is available for representing additive compounds by ring-symbols. A provisional method is adopted in this book for the few instances in which such representation is required. Additive elements or groups are indicated by placing the proper sign at a short distance from the angle and connected by a bond. There is also no uniform method of indicating cyclic combinations containing less than six carbon atoms nor those containing atoms of different elements (heterocyclic). A truncated hexagon is generally used for five-membered rings. For indicating the heterocyclic (pyridine) ring, C_5H_5N, the benzene hexagon with a small N close to an angle will be used in this book. This method is exemplified in the formula for the quinolines (see p. 182).

For illustration and comparison, the ring-symbols of a few compounds are given here. The substances are described in the following pages.

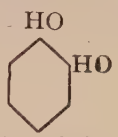
Hydroxybenzen
(Phenol)

Nitrobenzene

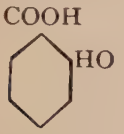
Carboxybenzene
(Benzoic acid)

Benzaldehyde
(Bitter-almond oil)

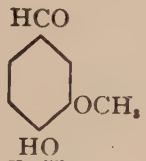
Benzyl alcohol



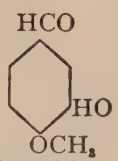
Resorcinol



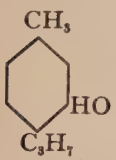
Salicylic acid



Vanillin



Isovanillin



Thymol

Sulphanilic acid
(1–4 aminobenzene-
sulphonic acid)

Homologues and Derivatives of Benzene.—Benzene is the first member of a series of the general formula C_nH_{2n-6} of which the following compounds are examples:

Benzene,	C_6H_6		
Toluene,	C_7H_8	$C_6H_5(CH_3)$,	methylbenzene
Xylene,	C_8H_{10}	$C_6H_4(CH_3)_2$,	dimethylbenzene
Cumene,	C_9H_{12}	$C_6H_3(CH_3)_3$,	trimethylbenzene
Cymene,	$C_{10}H_{14}$	$C_6H_2(CH_3)_4$,	tetramethylbenzene

Toluene is a colorless liquid, of sp. gr. 0.870. It boils at 110°. A substitution of one atom of the benzene-hydrogen of toluene must produce

three isomeric forms, since the substituting group must take a position either 1–2 (ortho), 1–3 (meta), or 1–4 (para), with reference to the methyl group, for, as the structural formula and systematic name of toluene indicates, it is not a seven-carbon chain but a substitution of methyl for one of the hydrogen atoms of benzene. The substitution may take place in the methyl group. This is termed "*side-chain*" substitution and gives rise to bodies which show, in empirical formulas, isomerisms with the ordinary benzene substitutions.

Methyl-benzene
(Toluene)

Hydroxytoluene, $C_6H_4(HO)(CH_3)$, of which there are three forms is isomeric but not identical with $C_6H_5CH_2HO$. The latter is *benzyl alcohol*. For structural formula see p. 167.

Nitrobenzene, $C_6H_5NO_2$.—This is easily prepared by the action of strong nitric acid on benzene. It is a colorless liquid, with an odor somewhat like that of essential oil of bitter almonds, for which it has been used as a substitute in flavoring soaps and cosmetics. It is known commercially as *oil of myrbane*. The reaction for its production is:

$$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$$

Aniline, Phenylamine, Aminobenzene, $C_6H_5NH_2$.—This is made by the action of nascent hydrogen on nitrobenzene, *e. g.*, by mixing nitrobenzene with tin and hydrochloric acid or with iron filings and acetic acid. The reaction is:

$$C_6H_5NO_2 + H_6 \rightarrow C_6H_5NH_2 + 2H_2O$$

Aniline is a liquid, boiling at 182°. It is an active poison. By the action of oxidizing agents it becomes converted into bodies of complicated composition, some of them having coloring powers of great beauty and variety, so-called "aniline or coal-tar colors." Crude aniline, commonly known as "aniline oil," contains homologous substances, such as toluidines (methyl aniline) and xylidins (dimethyl anilins).

Phenol, Hydroxybenzene, C_6H_5HO, *Carbolic acid, Phenic acid, Phenylic acid*.—This exists in coal tar, and can be made artificially by several

processes. It forms colorless crystals, deliquescent, and soluble in water, melting at 34° and boiling at 187°. It has an odor like that of creasote. It is sometimes called "coal-tar creasote." The commercial article usually has a pink tinge. Applied to mucous membranes, phenol promptly produces blanching and then an eschar. Strong alcohol is antidotal in action. The hydrogen in the hydroxyl of phenol can easily be replaced by positives yielding a series of compounds termed "phenates" or "phenylates." The sodium compound being readily soluble in water and less corrosive than phenol, is used as an antiseptic and as a wash for removing skin-parasites from domestic animals.

Benzaldehyde C_6H_5HCO, is volatile oil of bitter almonds. Its formation from amygdalin by a species of fermentation is pointed out elsewhere (p. 159). It is a colorless liquid, heavier than water, and, as usually made, has the smell of hydrogen cyanide since that body is formed from amygdalin at the same time as the benzaldehyde. Oil of bitter almonds has been used in confectionery as a flavor. It is sometimes substituted by nitrobenzene.

Benzoic acid, carboxybenzene, C_6H_5COOH, occurs in several resins, especially in *benzoin*, and can be made artificially by oxidation of toluene. It is a white crystalline solid, with faint odor and disagreeable taste. It dissolves but slightly in cold water, but more so in hot water and alcohol. It sublimes at a temperature below its boiling point. It is an antiseptic.

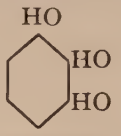
Sodium benzoate is a white crystalline solid with faint odor. It is soluble in water; the solution has a somewhat nauseous taste. It has marked antizymotic properties and is now used as a preservative in foods liable to ferment.

Benzyl alcohol, *Phenyl carbinol*, $C_6H_5(CH_2HO)$, is the true alcohol of this series. It is isomeric with the hydroxytoluenes (cresols) but entirely of a different nature and quite different in properties (see p. 167).

Resorcinol, *Resorcin*, *Metadihydroxybenzene*, $C_6H_4(HO)_2$ (for structural formula see p. 167). This can be obtained from the resins of galbanum and asafetida and also synthetically from several benzene derivatives. It is a colorless, crystalline body soluble in water, alcohol and ether. It is antiseptic.

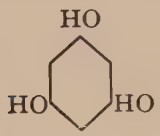
Pyrogallol, *Pyrogallic acid*, $C_6H_3(HO)_3$, 1–2–3 trihydroxybenzene, was originally obtained, as its name indicates, by heating gallic acid. It is a colorless, crystalline body, soluble in water. It absorbs oxygen from the air and decomposes. The action is especially rapid in alkaline solu-

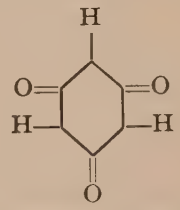
tion and is utilized in developing photographic negatives and in the analysis of gaseous mixtures containing free oxygen.



Pyrogallol

Phloroglucol, Phloroglucin, $C_6H_3(HO)_3$.—The molecule of this body is supposed to be tautomeric. The annexed formulas show two possible forms. One form is 1–3–5 trihydroxybenzene, the other form is termed triketohexamethene. Originally obtained from a glucoside, *phloridzin*,



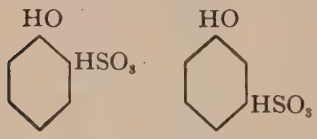


of certain root barks, it is now made from resorcinol. It is a colorless, crystalline body, soluble in water and alcohol. The alcoholic solution is used in mixture with a solution of vanillin for detection of hydrochloric acid in gastric juice.

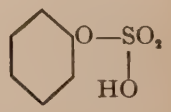
Phenolsulphonic acids, $C_6H_4(HO)\ (HSO_3)$.—Three are known. They are capable of forming salts, strongly antiseptic salts, which have been used as disinfectants.

Phenylsulphuric acid, Phenyl acid sulphate, $C_6H_5HSO_4$, is empirically isomeric with the phenolsulphonic acids but different in structure. Its potassium salt occurs in urine, and is one of the so-called *ethereal sulphates*, the formation of which is supposed to be dependent on the putrefactive processes taking place in the intestinal canal.

The structural formulas will show the relations of the four bodies.



Phenolsulphonic acids



Phenylsulphuric acid

Thymol (see structural formula p. 167), *isopropylmetahydroxytoluene*, is one of the ingredients of oil of thyme. It forms colorless crystals that melt at 50°. It has an odor recalling that of the oil of thyme. Thymol has marked antiseptic powers.

Guaiacol, 1–2 hydroxymethoxybenzene, $C_6H_4(HO)(CH_3O)$, is a mixed ether of phenyl and methyl with alcoholic hydroxyl also present. It is the important constituent of creasote from beechwood tar. When pure it is a white solid with but slight irritating qualities. Commercial guaiacol is a liquid, often very impure, and decidedly irritating to mucous membranes.

Vanillin (see p. 167) is the principal flavoring constituent of vanilla.

Picric acid, $C_6H_2(NO_2)_3HO$, is the *trinitrophenol* in which the nitro-groups are arranged symmetrically with regard to each other and to the hydroxyl. Picric acid is a deep yellow solid, soluble in water. It dyes silk and wool without a mordant and coagulates albumin. It is very bitter, a property to which the name refers. As the formula shows, it is not a carboxyl acid, but the nitro-groups give the hydrogen of the hydroxyl acid function. This hydrogen may be replaced by positives, forming salts, most of which are explosive.

Salicylic acid, oxybenzoic acid, $C_6H_4(COOH)(HO)$ (see p. 167), differs in formula from benzoic acid by an additional atom of oxygen. It is usually made from sodium salicylate obtained by the action of carbon dioxide on sodium phenate.

Sodium phenate Sodium salicylate

$$NaC_6H_5O + CO_2 \rightarrow NaC_7H_5O_3$$

Salicyclic acid forms colorless prismatic crystals, sparingly soluble in water. The solution produces a deep violet with ferric salts. It has high antiseptic qualities and is much used as a preservative in foods and beverages.

Methyl salicylate exists in the volatile oils of wintergreen and birch. By saponifying these and decomposing the product with strong acid, natural salicylic acid may be obtained. Salicylic acid has a marked restraining action on several starch-converting enzyms.

Cresols, $C_6H_4(CH_3)HO$, methyl phenols, cresylic acids. These have the same relation to toluene, C_7H_8, that phenol has to benzene. Phenol is hydroxybenzene; cresol is hydroxytoluene. They exist in coal tar. Three isomeric forms are known.

Lysol, now much used as a surgical antiseptic, is a mixture of the cresols saponified by caustic soda and thus rendered soluble in water.

Toluene, methyl benzene, $C_6H_5CH_3$, exists, of course, in but one form. It resembles benzene in many of its properties but has a marked antiseptic action and is used in preserving specimens for clinical examination. By treatment with nitric acid under certain condition a very high explosive, trinitrotoluene, commonly called TNT, is obtained. There are 6 possible forms, but only one is used as an explosive.

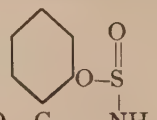
QUINONES.—The substitution of oxygen for hydrogen in the proportion of O_2 for H_2 (instead of for H_4, as usual) in closed-chain compounds, gives rise to a series of bodies termed *quinones*. Some of them are analogous in structure to hydrogen peroxide, and like it are active oxidizing agents. Two series have been obtained, representative of 1–2 and 1–4 substitutions. The latter series *true*, or *paraquinones*, are of the greater importance.

Quinone, benzoquinone is the type substance. It forms yellow crystals which have a penetrating disagreeable odor and irritate the skin.

Phthalic acids, dicarboxybenzenes, $C_6H_4(COOH)_2$.—These are the final products of the oxidation of side-chains of benzene derivatives. There are, of course, three forms: 1–2, 1–3, 1–4. The most important is:

Phthalic acid, $C_6H_4(COOH)(COOH)$ is 1–2 dicarboxybenzene. This is obtained by the oxidation of naphthalene, by which the extra ring is broken and its carbon converted in carboxyl. It is a colorless, crystalline body soluble in water (see diethyl phthalate, p. 134).

Saccharin, Benzosulphinide, $C_7H_5NSO_3$.—The structural formula shows the nature of this body. It is an imino-derivative of benzosulphonic acid. It is a white crystalline solid soluble in water; the solution is very sweet. Saccharin has been estimated as several hundred times as sweet as cane sugar. It has marked antiseptic powers, and is much used as a substitute for sugar and sometimes, as a preservative.

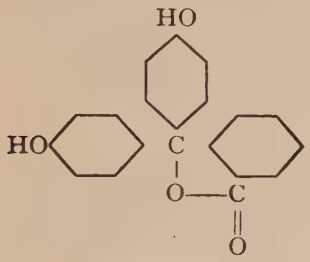


Saccharin

PHTHALEINS.—These are complex derivatives of phthalic acid. Some of them have acquired much importance on account of their value as dyes and indicators. The general nature of the structural formula is

shown by that for *phenolphthalein* given below. The phthaleins must not be confounded with the "*phthalins*," a less important group, not requiring special consideration here.

Phenolphthalein is a light yellow powder almost insoluble in water but freely soluble in alcohol. The solution is nearly colorless when neutral or acid, but becomes bright red when alkaline. It is much used as an indicator.



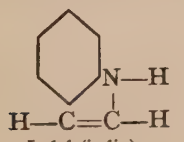
Phenolphthalein

Resorcinolphthalein, *fluorescein*, is a reddish powder which dissolves in strong alkaline solutions to produce a dark red solution, but when highly diluted the liquid shows a vivid green fluorescence.

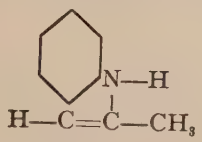
Eosins, Rhodamins.—These classes of colors, now well known on account of their use in coloring foods, beverages and confections, are derivatives of the phthaleins.

Indol, C_8H_7N.—The structural formula shows this to be a union of a pyrrol ring with a benzene ring. It is of considerable importance because of its occurrence among the products of putrefaction, and pancreatic digestion of proteins, and also its relation to the principal coloring matter of indigo.

Skatol is a methyl substitution of indol. It occurs with indol and is a characteristic ingredient of the contents of the intestinal canal.



Indol (indin)



Skatol (skatin)
(methyl indin)

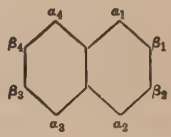
Indigotin, $C_{16}H_{10}N_2O_2$, the principal coloring matter of indigo, is a duplicated indol with substitution of two oxygen atoms for four hydrogen atoms. It exists in the indigo plant in the form of a glucoside, "indican," which is hydrolyzed by dilute acids or enzyms. The change can be brought about by exposing the macerated plant-tissues to air. Indigotin is insoluble in water.

Naphthalene, $C_{10}H_8$, often called *coal-tar camphor*, is obtained from coal-tar, in the form of white, somewhat fragrant, crystalline scales. It melts at 80°. It is slightly soluble in boiling water. It is used extensively to protect goods against moths and is an important source of synthetic indigo. Naphthalene consists of a double ring of carbon atoms saturated with hydrogen.

This formula is usually expressed by

which may be oriented in the same manner as the benzene ring, beginning at the upper right hand angle and numbering in the direction of the numbers on a clock.

or



A substitution of one atom of hydrogen in naphthalene may product two isomeric derivatives, depending on the position of the substituting body. Substitution at points, 1, 4, 5 or 8 are termed "alpha" derivatives; substitutions at 2, 3, 6 or 7 are termed "beta" derivatives. Each may be more definitely indicated as shown in one of the ring-symbols (see p. 175).

Naphthols, Hydroxynaphthalenes, $C_{10}H_7HO$.—When naphthalene is dissolved, in strong sulphuric acid, a mixture of alpha- and betanaphthalenesulphonic acids is obtained. If these be separated and saponified with sodium hydroxide, each will yield the corresponding hydroxide (naphthol). The two naphthols are much alike, being white, crystalline bodies, freely soluble in alcohol, sparingly in water and possessing marked antiseptic and germicide powers. Betanaphthol is almost exclusively used.

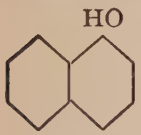
Betanaphthol, (*naphthol*), is a colorless crystalline powder, soluble in about 1000 parts of cold water, 75 parts of boiling water, very soluble in alcohol, ether, chloroform and alkaline solutions. It becomes slightly yellow on exposure to light. It is used as an antiseptic and preservative.

The naphthols yield sulphonic acids and nitro-derivatives exhibiting numerous instances of isomerism. A few of these are of considerably practical importance.

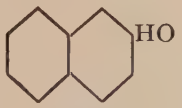
Dinitro-alphanaphthols.—One form is known as *Martius' yellow* and *naphthol yellow*. It is a bright yellow powder of high coloring power and has been used as a color for food and confections, but the fact that in large doses it produces functional disturbances has led to the prohibition of this use.

Naphthol yellow S, a sulphonated derivative of naphthol yellow, is a yellow powder of high coloring power, and being apparently much less active than the latter has displaced it as a food color.

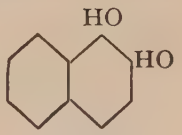
The following structural formulas show several naphthalene derivatives:



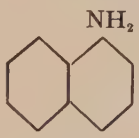
α-naphthol
α-hydroxynaphthalene



β-naphthol
β-hydroxynaphthalene



α-β-naphthol



α-amino-naphthalene

Anthracene, $C_{14}H_{10}$.—This is present in the higher-boiling portions of coal-tar. It crystallizes in colorless scales that show violet fluorescence. An important use is for the synthetic production of alizarin, the coloring matter of madder-root.

Benzidine, *diamidodiphenyl*, $(C_6H_4)_2(NH_2)_2$, belongs to the class of *polynucleated cyclic compounds*, that is, constituted of independent rings joined directly at one point, as contrasted with *duplicated* rings, such as naphthalene and phenanthrene, or *conjugated* rings such as phenyl ether, phenazin, anthracene and alizarin. It is employed as a test for distin-

guishing between raw and boiled milk; also see a test for blood. Information of these points will be found in the section on Clinical Chemistry.

Benzidin

COAL-TAR COLORS

The coal-tar colors are a very numerous group of compounds obtainable from the hydrocarbons present in the tar. They are all closed-chain derivatives, but not all from benzene. The first color discovered was a violet which Perkin obtained, in 1856, while experimenting with aniline. Hofmann (1859) produced a brilliant red, magenta, from aniline, and the following year the manufacture of it was begun. From that date the number rapidly increased and they began to displace the natural colors. In 1868 alizarin, the coloring matter of madder, was obtained by synthesis from anthracene and indigo has been made from naphthalene.

On account of the almost exclusive use of crude aniline in the manufacture of these colors in the early period, they were termed "aniline colors," a name which is still largely applied, although some of the most used colors are not made from aniline or its immediate derivatives.

As a class these bodies are brilliant in tint, of high coloring power and soluble in water and alcohol. They include every known shade and have to a great extent replaced the natural dyes. They are much used for coloring foods, beverages and household articles, and their sanitary relations have been the subject of much investigation and discussion.

Their composition is, as a rule, very complex, but as nearly all of them are produced from simple substances (*e. g.*, benzene, naphthalene, anthracene) by synthetic methods, the structural formulas are mostly known. The commercial colors include representatives of all the larger groups of closed-chain derivatives. The important ones are considered in connection with the groups to which they belong.

As the systematic names of these bodies are generally long and awkward, they are almost always known by commercial titles which are arbitrary and often fanciful. Abbreviations are used to indicate shade, special condition or manufacturer. A few of these abbreviations are here noted:

Letters such as J, JJ, BB, OO are descriptive of the shades. Eosin J indicates an eosin with a yellow shade (Fr. *jaune*); German chemists often use G for this. JJ means a stronger yellow shade; OO a strong orange shade. S generally means sulphonation; naphthol yellow S is the sulphonated derivative of naphthol yellow. BASF (Badische Anilin und Soda Fabrik) is an example of a manufacturer's name.

A few of these colors are insoluble in water. Some azo-colors insoluble in water are soluble in oils, to which they impart an orange or yellow tint. They are now often used in coloring fatty foods, especially butter and cheese. Many colors are affected by acid or alkaline solutions and are used as indicators.

Rosaniline.—This is produced whenever crude aniline which always contains toluidine (methylanilines), is treated with oxidizing agents. Arsenic acid, nitrobenzene and mercuric nitrate are the oxidizing agents practically used. The arsenic acid method was the first, and hence all the rosaniline products were liable to contain arsenic.

Rosaniline forms salts with acids, some of which are important dyes. One of these is *magenta, fuchsine, aniline red, rosaniline hydrochloride.* It is soluble in water, producing a brilliant red solution of high coloring power. It is used largely for coloring foods and beverages. The name "magenta" is an interesting instance of the fanciful source of these color names. It refers to the battle at Magenta, Italy, fought in the year in which the color was first prepared.

Methylene Blue, $C_{16}H_{18}N_3SCl$.—This is a complicated sulphur derivative, which has been used as a therapeutic agent and also for staining pathologic and bacteriologic preparations.

Methyl violet, $C_{24}H_{28}N_3CL$ is a product of oxidation of dimethylaniline. It is of very high coloring power and is also an antiseptic.

TERPENES

The *terpenes* are cyclic hydrocarbons having the general formula $(C_5H_8)_n$. When oxidized they form camphors and resins. They may be considered as cyclic compounds in which one or more latent valencies exist.

Many *essential oils* consist almost entirely of terpenes, others of a mixture of terpenes with oxygenated bodies. The terpenes are capable of polymerization, and often show optical activity. The natural forms are sometimes composed of equivalent proportions of *d* and *l* modifications.

The following classification is based upon the differences in their molecular weights:

1. Hemiterpenes, C_5H_8
2. Terpenes, $C_{10}H_{16}$
3. Sesquiterpenes, $C_{15}H_{24}$
4. Diterpenes, $C_{20}H_{32}$
5. Polyterpenes, $n(C_{10}H_{15})$

Pinene, $C_{10}H_{16}$, constitutes the principal portion of oil of turpentine. It is a colorless liquid possessing an aromatic odor. It unites with hydrochloric acid to form pinene hydrochloride, $C_{10}H_{17}Cl$, which, from its resemblance in physical properties to camphor, has been called "artificial camphor." When oil of turpentine is mixed with alcohol and nitric acid and allowed to stand for several days, a crystalline compound separates which has the composition $C_{10}H_{18}(OH)_2 + H_2O$, and is known as *terpin hydrate*.

Camphene, $C_{10}H_{16}$, is a white crystalline solid, which can be oxidized to form camphor.

Limonene, also known as *hesperidene*, *carvene* and *citrene*, constitutes almost the entire portion of several of the volatile oils, notably oil of orange peel. Oil of lemon peel consists of a mixture of pinene and limonene. Many of the volatile oils such as orange and lemon, consisting almost entirely of terpenes, lose their characteristic odor upon standing and acquire the odor of oil of turpentine, the change being due to some obscure molecular re-arrangement.

Terebene is a mixture of several of the terpenes (pinene, terpinene and dipentene) and is produced by the action of sulphuric acid on oil of turpentine.

Polyterpenes $(C_{10}H_{16})_x$, exist in caoutchouc and gutta percha and may be formed by the polymerization of oil of turpentine.

CAMPHORS

The *camphors* are oxygenated derivatives of the terpenes. They are sometimes called *stearoptenes* to distinguish them from the *eleoptenes* or liquid portions of the volatile oils in which they usually occur. Some are alcohols while others resemble the ketones.

Ordinary *camphor*, $C_{10}H_{16}O$, *Japan camphor*, is obtained by distilling the wood of a species of cinnamon in a current of steam. It is a crystalline solid, possessing a characteristic odor and a pungent, afterward a cooling, taste. With bromin, camphor forms a derivative known as *monobromated camphor*, $C_{10}H_{15}BrO$.

Borneol or *Borneo camphor* is $C_{10}H_{18}O$, from the wood.

Linalool, $C_{10}H_{17}OH$; *Geraniol*, $C_{10}H_{17}OH$; *Citral*, $C_{10}H_{16}O$, and *Citronellal*, $C_{10}H_{20}O$, are odorous bodies belonging to this class, obtained from certain volatile oils, *citral* being present in oil of lemon.

Menthol, $C_{10}H_{20}O$, is obtained from volatile oils of peppermint. It forms colorless, needle-shaped crystals melting at 46° having a warm mint-like taste.

Essential Oils.—These, often called *volatile oils*, are the complex proximate constituents to which the characteristic odors of plants are due. They are obtained from flowers, seeds, leaves, stems, barks and roots, mostly by distillation with water, the volatile oil passing over with the steam and condensing with it. Some of the aromatic waters used in medicine, such as rose water and orange-flower water, are obtained as by-products in the distillation of the essential oils. The essential oils are usually mixtures of terpenes and camphors, although some consist of esters, aldehydes or ketones.

Essential oils are distinguished by their complete volatility, comparative insolubility in water and complete solubility in alcohol, ether, chloroform and similar solvents. They may be:

Terpenes: Oils consisting mainly of members of the class of terpenes, as oil of lemon.

Oxygenated: Oils consisting of aldehydes, esters or ketones often associated with small amounts of terpene, as oil of cinnamon.

Sulphurated: Containing sulphur, as oil of mustard.

Nitrogenated: Containing nitrogen, as oil of bitter almond.

Oil of turpentine is obtained by the distillation of the oleoresin of a species of pine; it consists almost entirely of pinene.

Resins.—These are also products resulting from the oxidation of the terpenes and are associated in plant tissues with other proximate principles, such as volatile oils and gums. They usually exhibit the characters of acids or anhydrids and are decomposed by strong heat. They are divided into three groups: 1. true resins; 2. oleoresins; 3. gum-resins.

The hard or true resins, of which ordinary resin or colophony (sometimes called rosin) is a type, are fusible solids capable of crystallization under favorable conditions, insoluble in water, but soluble in alcohol.

Colophony or common resin is obtained as a residue when the oleoresin of the pine tree is distilled for obtaining oil of turpentine. It consists largely of abietic anhydrid, $C_{44}H_{62}O_4$, which is converted into abietic acid by the action of alcohol and water.

Crude turpentine, Burgundy pitch and *Copaiba* are natural oleoresins, the consistency being liquid or semi-solid according to the amount of volatile oil associated with the resin.

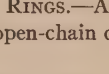
Balsams are oleoresins which are associated with aromatic products, such as benzoic or cinnamic acid. The principal balsams are *Benzoin, Balsam Peru, Balsam Tolu* and *Storax*, all of which are used in medicine.

HETEROCYCLIC COMPOUNDS

The closed chains so far described are assumed to contain only carbon atoms. Many compounds are known in which the ring consists of carbon atoms with an atom of oxygen, sulphur or nitrogen. These are termed *heterocyclic compounds*. Nitrogen carries with it one hydrogen atom (see Pyrrol).

The following is a synopsis of the most important groups of this type:

THREE-MEMBERED RINGS.—Among these are found bodies which might be classed as open-chain compounds, such as ethene oxide, C_2H_4O, of which the structural formula must be:



FOUR-MEMBERED RINGS.—In these is included betaine.

FIVE-MEMBERED RINGS.—These include several important types of compounds.

Furfurane: four carbon and one oxygen atom.

Thiophene: four carbon and one sulphur atom.

Pyrrol: four carbon and one nitrogen atom.

Of the very many derivatives that these bodies may yield, only a few of special importance can here be noted.

Furfurane, C_4H_4O, is present in the materials collected from the distillation of pine wood. It is of less interest than its aldehyde.

Furfural, $C_4H_3(HCO)O$, often termed furfurol, is produced in the destructive distillation of, or action of strong acids upon, bodies containing carbohydrates, and in small amount in alcoholic fermentation.

Coumarin.—This is a crystalline principle existing in the tonka bean. Its odor is sufficiently like that of vanillin to cause the tonka bean to be used very much as a substitute for vanilla.

Thiophene, C_4H_4S, may be regarded as benzene in which two atoms of carbon are replaced by sulphur. The principal interest attaching to it is that it is a frequent impurity of benzene.

Pyrrol, C_4H_4NH, is found in bone oil and coal-tar. It is a colorless liquid with an odor recalling that of chloroform.

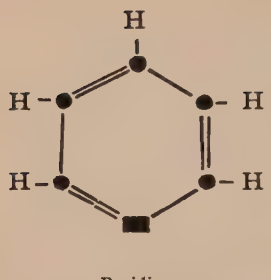
According to the system of nomenclature now in vogue the termination "ol" is not appropriate to this compound. The name "pyrrin" would be more systematic.

Six-membered Rings, Pyridines.—This is a series of bodies that contain nitrogen atoms in a closed chain with carbon atoms. This grouping, known as the "pyridine ring," is a stronger molecular linking than even benzene, and the opportunities for isomerism are also greater than with benzene. The type compound is:

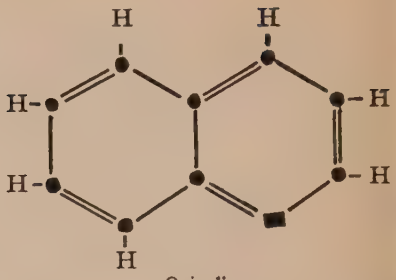
Pyridine, C_5H_5N.—This was first noted in the offensive liquor obtained by distilling bones, formerly used in medicine under the name "Dippel's animal oil." It is found in coal-tar. Pyridine is a liquid with a disagreeable odor, boiling at a temperature somewhat above that of boiling water. It is a monacid base combining, as is usual with nitrogen bases, with the entire acid molecule. It is used as a denaturant for alcohol.

Quinoline.—The pyridine ring associated with a benzene ring gives rise to quinoline, which bears the same structural relation to pyridine that naphthalene does to benzene. The structural formations of these two bodies are shown in the annexed drawings in which the atoms are represented by special signs. It is to be noted that while pyridine cannot exist in more than one form, since the nitrogen atom may be placed at any angle of the chain without altering the relations of the other atoms to it, the quinoline group is capable of two modifications as shown. Pyridine and quinoline contain no asymmetric carbon and, therefore, do not have optical activity.

Quinoline is a colorless liquid of high dispersive power. It is produced in the destructive distillation of coal, bones and many alkaloids. Pyridine and quinoline are of much interest not only on account of the large number of derivatives they yield, but principally because the molecular structure is present in many alkaloids.



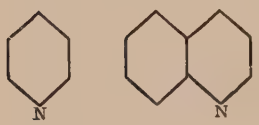
Pyridine



Quinoline

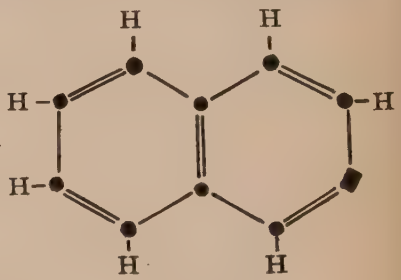
The round dots represent carbon atoms; the rectangular represent nitrogen atoms. (Diagrammatic formulas.)

There is as yet no uniform method of representing the pyridine ring. In this book it is represented by benzene ring-symbol with a small "N" attached close to one of the angles, as shown in the annexed formula:



Pyridine symbol $= C_5H_5N$

Quinoline symbol $= C_9H_7N$



Isoquinoline

Homologous Derivatives.—The hydrogen of all these molecules may be replaced by the alkyl radicals, thus forming homologous series.

Additive Compounds.—As with benzene and naphthalene the latent valencies of these closed chains may be developed, and a series of derivatives obtained in which the original hydrogen is not disturbed.

Piperidin, Pyridine hydrid, $C_5H_{11}N$, is closely related to conine.

Conine is a substitution of propyl (trityl), C_3H_7, for the additive hydrogen atoms in piperidin nearest to the nitrogen, and is therefore, 1-2 propylpiperidin. The introduction of the alkyl radical makes the carbon atom to which it is attached asymmetric. Conine is known to exist in three forms, *d*, *l* and inactive. The natural conine is the *d*-form rotatory.

Piperine.—This substance is an abundant ingredient of all forms of pepper. Its empirical formula is identical with that of morphine, but it is not an alkaloid, and is structurally wholly different from morphine.

Organo-metallic Compounds

Notwithstanding the fact that in the great mass of reactions of organic chemistry the metals are not found combining with carbon, a large number of such associations can be prepared by special methods. The first was obtained many years ago by a French apothecary who distilled arsenous oxide with potassium acetate, and obtained a poisonous fuming liquid. The nature of this was ascertained much later, when Bunsen found that the principal product is arsendimethyl oxide $As(CH_3)_2O$. From this he obtained a large number of derivatives, which he called the "cacodyl" compounds from two Greek words meaning "bad principle," from their poisonous qualities.

Compounds of some of the common metals, such as zinc, mercury, and lead, with the hydrocarbon radicals have been obtained in large number. Zinc ethyl $Zn(C_2H_5)_2$ is one of these. The most important compound of this type is

Tetrethyl lead, $Pb(C_2H_5)_4$ which has come into extensive use as an "anti-knock" addition to gasolin. It is a heavy liquid, very poisonous. It is used in the gasolin in association with ethylene bromide, $C_2H_4Br_2$.

Arseno-organic Compounds.—Special attention has been given to this class of compounds on account of the value of some of them for treating diseases due to the presence of minute animal organisms in the blood. Most of them are derivatives of benzene. They have received trade names which give little or no information as to their structure. The first introduced widely as designated 606, having been the 606th substance prepared in a certain research. Salvarsan, arsphenamine and neo-arsphenamine are some of the names now in vogue. The formulas are complicated and the details of them belong to therapeutics and materia medica.

COMPOUNDS CONTAINING NITROGEN

CYANOGEN AND DERIVATIVES

Cyanogen is CN. It combines with both negative and positive bodies. Thus both KCN and CNCl are known. The former is potassium cyanide; the latter cyanogen chloride.

Two forms of cyanogen compounds are known, cyanides and isocyanides

Potassium cyanide	Potassium isocyanide
K—C≡N	C≡N—K

In the former nitrogen is triad, in the latter, pentad.

Potassium Cyanide, KCN.—This is a snow-white mass, very soluble in water, and easily decomposed even by the carbonic acid of the air, hydrogen cyanide being formed. It dissolves many silver compounds that are insoluble in water, and is used in making solutions for silver-plating and in photography, also in very small doses as a medicine. It is an active poison. Oxidizing agents convert it into potassium cyanate.

Hydrogen Cyanide, HCN.—This is generally called *hydrocyanic* or *prussic acid*. It is a colorless liquid, easily decomposed and intensely poisonous. As sold for medical purposes, it is very dilute, consisting of 2 parts of acid to 98 of water. It has, even when much diluted, a strong odor suggesting bruised peach kernels; in fact, hydrogen cyanide is formed from these substances by the decomposition of nitrogenous principles when the seeds are crushed with cold water. This occurs under the influence of enzyms, for if these are first coagulated by boiling alcohol, no decomposition occurs. The reaction by which it is formed when bitter almonds are macerated with water consists in the hydrolysis of a crystalline principle called *amygdalin*, under the influence of an enzym called *synaptase:*

Amygdalin		Benzaldehyde	Hydrogen cyanide	Dextrose
$C_{20}H_{27}NO_{11}$	$+ 2H_2O \rightarrow$	C_7H_6O	$+ HCN +$	$2C_6H_{12}O_6$

Hydrogen cyanide may also be made by decomposing other cyanides by strong acids, thus:

$$2KCN + H_2SO_4 \rightarrow K_2SO_4 + 2HCN$$
$$AgCN + HCl \rightarrow AgCl + HCN$$

Complex Cyanides.—The potassium group cyanides show a great tendency to combine with other cyanides, especially those of the iron group, to form complex cyanides, in which some properties of the simpler cyanides, especially the poisonous qualities, are much diminished. The iron series is the most important. Two well-marked compounds are known.

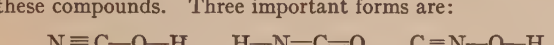
Potassium ferrocyanide, $K_4C_6N_6Fe$, often called *yellow prussiate of potash*, forms lemon-yellow crystals, which are not actively poisonous. Oxidizing agents convert it into:

Potassium ferricyanide, $K_3C_6N_6Fe$, commonly called *red prussiate of potash*. It forms large ruby-red crystals, soluble in water.

These compounds ionize, but the iron remains in the *negative* ion, hence the solution cannot respond to the ordinary tests for that element. On the other hand, they are delicate tests for iron when in the positive ion. See p. 96. Note also that a ferricyanide is produced by removing one atom of potassium and the action is called "oxidation," although no oxygen is concerned. See p. 44.

Nitroprussic Acid.—By the action of nitric acid upon potassium ferrocyanide, an acid-like body is formed, the structure of which is not understood. It is provisionally termed nitroprussic acid. Its importance lies in the fact that its sodium salt, $Na_2Fe(CN)_5NO$, generally called *sodium nitroprusside*, is a test for sulphur and for formaldehyde.

Cyanogen Hydroxides, Cyanic Acids.—Cyanogen units with hydroxyl to form several compounds that have the same percentage composition, but some are stereo-isomers, others polymers. Both forms of cyanogen form these compounds. Three important forms are:



Cyanic acid — Isocyanic acid — Fulminic acid

Cyanuric acid, $H_3C_3N_3O_3$, is of more complex structure. Fulminuric acid has the same empirical formula as cyanuric acid, but is a nitro-derivative and, therefore, of entirely different type.

The important derivatives of these acids are the cyanates and fulminates.

Potassium Cyanate.—The common cyanate is isocynate, KNCO. It exists in considerable amount in commercial potassium cyanide.

Ammonium cyanate, NH_4NCO, is of interest because it may be transformed by heating into urea $(NH_2)_2CO$. This transformation was the first instance of organic synthesis and its accomplishment broke down the lines between organic and inorganic chemistry. The change is a rearrangement as follows:

Ammonium cyanate — Urea

Fulminates.—As the name indicates, many of these are explosive. *Mercuric fulminate*, $Hg(CNO)_2$ explodes violently on percussion, and is the material used in percussion caps for firearms.

Silver fulminate, AgCNO, is more explosive than the mercuric salt.

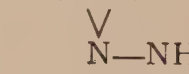
Thiocyanates.—These are often called *sulphocyanates.*

The soluble thiocyanates produce with ferric compounds a bright red solution of ferric thiocyanate, a delicate test for ferric compounds. No color is produced with ferrous compounds.

The known esters of thiocyanic acid are of the isothiocyanic type. They are sometimes termed "mustard oils," as the volatile oil of black mustard is allyl isothiocyanate $(C_3H_5)NCS$. As noted elsewhere, it does not exist in the seed, but is produced by a decomposition under the influence of a special enzym.

Azoimide, Hydrazoic Acid.—An interesting connecting link between inorganic and organic chemistry is furnished by this substance. It has the empirical formula N_3H. The structural formula is considered to be:

Azoimide
(Hydrazoic acid)



Ammonium hydrazoate

The acid is a colorless mobile liquid of disagreeable odor, and highly explosive. Its ammonium salt, NH_4N_3, has the empirical formula H_4N_4.

AMMONIUM DERIVATIVES

Amines and Amides.—Amine, NH_3, ammonia, is generally found among the products of decomposition of nitrogenous matter. One of the most striking properties of ammonia is its power to neutralize acids. When certain organic bodies containing nitrogen were found to have a similar property, a similar constitution was assigned to them. Morphine and quinine are decidely alkaline, and contain considerable nitrogen and were, therefore, regarded as ammoniacal. Many synthetic substances can be produced by the substitution of the hydrogen or nitrogen in ammonia, NH_3, or ammonium, NH_4, by different elements or radicals. The number of compounds so produced is greatly increased by the fact that these molecules are capable of polymerism, so that one set of compounds may be formed on the type NH_3, and another on that of N_2H_6, and so on. A very complete and systematic nomenclature has been adopted for these compounds. In the first place, the character of the replaceable radicals, and, to a certain extent, therefore, the character of the compound itself, is indicated by the termination. When the radical is positive, and especially

when it does not contain oxygen, "*ine*" is used; when it is negative and contains oxygen, "*ide*" is often used. When the nitrogen is replaced by some other member of its group (B, P, As, Sb and Bi), some distinct syllables of these names are added. The names of all the radicals entering into the compound are attached. If the molecule is duplicated, the syllabes "*di*," "*tri*," etc., are used to indicate the degree of duplication. If the compound is derived from the type NH_4 it has the termination "onium." The following list will show all these points:

NH_3, amine; N_2H_6, diamine; N_3H_9, triamine; N_4H_{12}, tetramine.
PH_3, phosphine; P_2H_6, diphosphine.
AsH_3, arsine.
SbH_3, stibine.
NH_4, ammonium; N_2H_8, diammonium; N_3H_{12}, triammonium.
PH_4, phosphonium.
AsH_4, arsonium.
SbH_4, stibonium.

The polymerization of the molecules takes place by introduction of radicals of dyad or higher valency. An alcoholic solution of ammonia and ethyl iodide heated for some hours in a sealed tube, gives the reaction:

$$NH_3 + (C_2H_5)I \rightarrow (C_2H_5)H_3NI$$

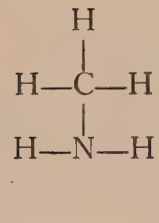
As NH_4I is ammonium iodide so the above compound is called ethylammonium iodide. By further action the whole of the hydrogen may be replaced by ethyl, and we get $(C_2H_5)_4NI$, tetrethylammonium iodide. Each of the hydrogen atoms may be replaced by a different radical, by which great complexity in structure and nature arises. Thus:

$(C_2H_5)_2(C_5H_{11})HNI$ ..... diethylpentylammonium iodide.
$(C_2H_5)_3(C_5H_{11})NI$ ..... triethylpentylammonium iodide.
$(CH_3)\ (C_2H_5)\ (C_3H_7)\ (C_4H_9)NI$ ..... methylethylpropylbutvlammonium iodide.

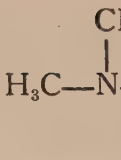
From NH_3 we may derive:

$(C_2H_5)H_2N$ ..... ethylamine.
$(C_2H_5)_2HN$ ..... diethylamine.
$(C_2H_5)_3N$ ..... triethylamine.

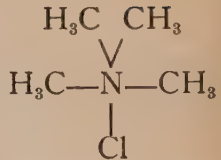
When but one-third of the hydrogen is substituted, the body is said to be *primary;* when two-thirds are substituted, it is *secondary;* when all is substituted, the body is *tertiary*. Ethylamine for instance, is a primary monamine. The following structural formulas show some of these bodies:



Methylamine



Trimethylamine



Tetramethylammonium chloride

Diamines and Diammoniums.—These always contain N_2:

$(C_2H_4)H_4N_2$.....ethenediamine (ethylenediamine).
$(C_2H_4)H_6N_2(HO)_2$.....ethenediammonium hydroxide.

Triamines, and triammoniums, tetramines and tetrammoniums, are formed on the same principle.

The following formulas show some of the compounds obtained by these elaborate substitutions and when the nitrogen is replaced by other members of its group:

Ethyl phosphine	Diethyl phosphine	Triethyl phosphine
$(C_2H_5)H_2P$	$(C_2H_5)_2HP$	$(C_2H_5)_3P$
Trimethyl arsine	Tripentyl stibine	Triethyl bismine
$(CH_3)_3As$	$(C_5H_{11})_3Sb$	$(C_2H_5)_3Bi$
	Triethyl borine	
	$(C_2H_5)_3B$	

Tetrethylphosphonium hydroxide $P(C_2H_5)_4HO$

Tetrethylstibonium iodide $Sb(C_2H_5)_4I$

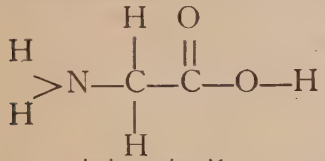
Several complex amines are used in medicine. Among these is:

Hexamethenetetramine $(CH_2)_6N_4$, which is made by adding ammonium hydroxide to formaldehyde. The reaction is a dehydrolysis:

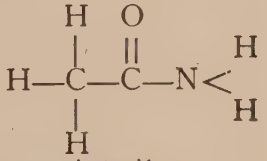
$$6CH_2O + 4NH_4HO = (CH_2)_6N_4 + 10H_2O$$

The product is a colorless, almost inodorless, crystalline mass, soluble in water. It is now sold under proprietary names—*e. g.*, formin, cystogen, urotropin—for the treatment of purulent affections of the kidneys and bladder. When taken internally it is partly decomposed into formaldehyde and ammonium hydroxide. The former is largely excreted by the kidneys and thus exercises its antiseptic action over the mucous membranes of the genito-urinary tract.

Amides.—All primary monamines may be expressed as substitutions of amidogen, NH_2, for other monads. When the amidogen is associated with a substantially positive group, the compound is basic and is called an amine, but when associated with negative groups it may form either acid or neutral bodies which are often called amides, but this term is going out of use. Thus, amidogen may be substituted for the hydrogen benzene, giving rise to $C_6H_5NH_2$, aminobenzene, which is basic, and is therefore an amine. Substituted for the hydrogen of acetic acid it gives aminoacetic acid, in which some of the acid properties are retained; but substituted for the hydroxyl of acetic acid it entirely removes the acid function, forming a body called acetamide. These facts are shown by structural formulas:

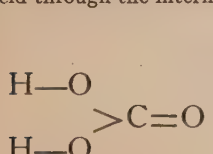


Aminoacetic acid

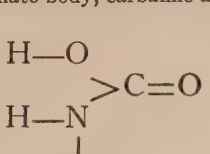


Acetamide

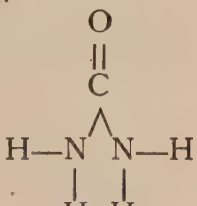
Urea, $(NH_2)_2CO$, is the most abundant solid ingredient of normal human urine. It is a colorless solid, crystallizing readily and is freely soluble in water and alcohol. Most of its salts are also soluble, but the nitrate and oxalate are but sparingly so, hence the addition of nitric or oxalic acid to urine rich in urea will produce a precipitate. Urea is strictly a diamide, that is, formed by the substitution of an acid radical—the group CO—but this overcomes only one of the amidogen groups, hence urea forms salts with one equivalent of acid, not as do the diamines with two equivalents. As with all other compounds of these types, the whole molecule of the acid acts; urea hydrochloride is CH_4N_2O, HCl. The following structural formulas will show the relation of urea to carbonic acid through the intermediate body, carbamic acid:



Carbonic acid



Carbamic acid



Urea

Urea is not liable to decomposition when in pure solution, but in presence of protein matters and exposed to the air it soon hydrolyzes to ammonium carbonate. This is the ordinary reaction by which urine becomes alkaline on standing:

$$CH_4N_2O + 2H_2O = (NH_4)_2CO_3$$

This change is due to enzyms formed by microbes. It can be brought about rapidly by the action of a catalyst (enzym) called "urease," which is derived from a seed and is now a commercial article. This reaction is used for the determination of urea. (See under Clinical Chemistry.)

Urea is decomposed by hypochlorites and hypobromites with evolution of carbon dioxide and nitrogen.

Many substances of these types are found in the fluids of living tissues and among products of putrefaction. Some of these are described in the section on Purins, others in the section on Ptomaines. Others of importance are:

Taurin, aminothysulphonic acid, $C_2H_4(NH_2)HSO_3$, from bile. It forms colorless crystals very soluble in water. As it contains NH_2 and HSO_3 it has both acid and basic properties.

Aminoacetic acid, glycocoll, glycin, $HC_2H_2(NH_2)O_2$.—This is a crystalline solid, soluble in water; the solution has a sweetish taste. It is both an acid and a base. It easily forms salts with ordinary positives and also combines with common acids forming, for example, the following compounds: $CuC_2H_4NO_2$ and $C_2H_5NO_2HCl$, both of which are crystalline bodies.

Aminoacetic acid forms esters with the alkyl radicals and also amine derivatives of which the following will serve as examples:

Ethyl aminoacetate, $C_2H_5C_2H_4NO_2$.—This is a volatile liquid with an odor resembling that of cacao.

Hippuric Acid, Benzoyl Glycocoll.— The structural formula of this shows that it contains residues of both aminoacetic acid and benzoic acid; in fact, its empirical formula may be obtained by adding the formulas of these acids and deducting H_2O. By hydrolysis and also by the action of acids or alkalies, hippuric acid may be decomposed into benzoic acid and aminoacetic acid. As hippuric acid occurs in considerable proportion in the urine of herbivorous animals, it has been a commercial source of benzoic acid.

Trimethyl glycocoll is *betaine*, a ptomaine described in another section.

Amino-derivatives of the higher acids exhibit numerous instances of isomerism. Among these are:

Leucins.—Under the name leucins several analogous substances with the empirical formula, $C_6H_{13}NO_2$, have been included. They are found among the products of digestion of protein, especially under the influence of trypsin, and are often associated with tyrosin.

One form of leucin, an aminocaproic acid, is derived from casein and has also been prepared synthetically; another form is a derivative of butylacetic acid. Some of these forms contain asymmetric carbon and are, therefore, optically active.

Tyrosin, 1–4 Phenolaminopropionic Acid.—This is produced in many transformations of protein matters, such as boiling horn, hair or albumin with sulphuric acid, digesting proteins for some time with pancreatic secretion and by putrefactive actions.

Cystin, $C_6H_{12}N_2O_4S_2$, probably an aminothiolactic acid derivative occurs as a crystalline sediment in human urine and sometimes forms a calculus.

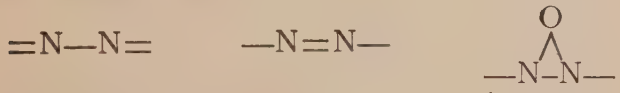
Asparagin is an example of the presence of amidogen in two positions in a molecule. It is succinic acid with one hydroxyl group replaced by amidogen, and another amidogen group replacing a hydrogen atom attached to carbon so that both the amine and amid structures are exhibited. *Asparagin* has asymmetric carbon. It is found in the seeds of many plants and in the sprouts of asparagus and vetch.

Asparagin occurs in both the *d* and *l* forms.

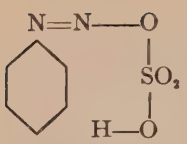
Purins, Alkaloids, Ptomaines.—These are groups of nitrogenous compounds many of which are amines or amides. The important bodies of each type are described in connection with the group named.

AZO-, DIAZO AND HYDRAZO-COMPOUNDS

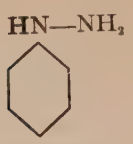
When two atoms of nitrogen are joined by two bonds, and the remaining bonds are joined to similar radicals, a group is formed called an *azo-compound.* When the radicals are dissimilar, a *diazo-compound* (*diazonium*) is formed. When an atom of oxygen is inserted between the nitrogen atoms, an *azoxy-compound* is formed. When one bond of each nitrogen atom is united to an atom of hydrogen, the body is called a *hydrazo compound.* These points are exemplified in the following formula:



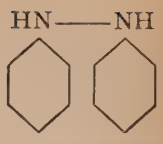
Hydrazo-group Azo-group Azoxy-group



Diazobenzene (diazonium) sulphate



Phenylhydrazine



Hydrazobenzene

Hydrazines.—The hydrazines agree with the diazo-compounds in containing dissimilar radicals, but differ in the fact that the union between the nitrogen is by one bond only.

The difference is shown in the following formulas:

Diazo-benzene nitrate $C_6E_5N = N—(NO_3)$

Phenylhydrazine nitrate $C_6H_5N—N(NO_3)$ (H H$_3$)

Azo-compounds are now of considerable practical importance. Many of them are brilliant in color and less liable to fade than some of the other forms of synthetic colors. Some of them have the valuable property of dyeing cotton without a mordant.

A few of the azo-colors are insoluble in water but soluble in alcohol and in oils. They are used for coloring fatty foods, especially butter and butter substitutes.

Methyl Orange, *Helianthin*, Porrier's *Tropeolin D*, *Orange III*, *Gold Orange*, *Mandarin Orange*.—Sodium dimethyl 1–4 amino-azobenzene-sulphonate. This series of commercial synonyms is given merely as an instance of the nomenclature of these bodies.

Bismarck brown is the hydrochloride of a complex azo-derivative. It is used for coloring imitation wines, fruit juices and in confectionery, as well as in dyeing textiles.

Congo Red.—This color belongs to a group termed "tetrazo-compounds" because they contain the azo-group twice. The term diazo is appropriated to a special form of azo-compounds. The tetrazo-compounds are chiefly interesting to dyers, but Congo red, is used in the laboratory as an indicator, having the striking property of assuming colors the reverse of litmus and other common vegetable colors. Congo red is blue in acid solution and red in alkaline. It is not a very delicate indicator, but is used in testing stomach-contents for free hydrochloric acid. It dissolves in water. It is used generally in the form of test-papers.

Diazo-compounds.—As previously noted, this term is applied when the nitrogen atoms are united by more than one bond and the residual bonds

are not in union with the same type of radical. The exact nature of the molecular structure has been disputed among chemists. Present opinion tends to regard them as more closely analogous to ammonium than to amine, and hence they are often termed "diazonium" compounds. The difference between these views is shown in the formulas for diazobenzene chloride:

Amine type

$$C_6H_5N = N—Cl$$

Ammonium type

$$C_6H_5—\overset{\overset{\|\|}{N}}{N}—Cl$$

These compounds are generally unstable. Many of them are explosive and some highly poisonous. It has been thought that some are formed in the putrefaction of proteins, especially milk proteins, and that this accounts for the violently poisonous properties of some spoiled foods. They do not appear to be present in advanced states of putrefaction, but when the food is merely stale. As they are mostly easily decomposed by heat, cooking of such food often takes away the poisonous action. The products will differ with different conditions. The small amounts in which the bodies are produced, and the ease with which they are decomposed, makes identification of them uncertain.

Diazo-compounds react with amino-compounds to produce complex substances, many of which have high coloring power. One of these reactions is used as a test for nitrites in water. It is made by adding sulphanilic acid (see p. 167) to alpha-amino-naphthalene (see p. 175). In the presence of nitrites a pink solution is produced. The test is very delicate. The reactions are:

$$\underset{\text{Sulphanilic acid}}{C_6H_4NH_2HSO_3} + HNO_2 \rightarrow \underset{\substack{\text{Diazobenzene}\\ \text{Sulphonic anhydride}}}{C_6H_4N_2SO_3} + 2H_2O$$

$$\underset{\substack{\text{Alpha-amino-}\\ \text{naphthalene}}}{C_6H_4N_2SO_3} + C_{10}H_7NH_2 \rightarrow \underset{\substack{\text{Alpha-azo-amino-naph-}\\ \text{thalenepara-azo-benzene}\\ \text{sulphonic acid}}}{C_{10}H_7(NH_2)N = NC_6H_4HSO_3}$$

The reactions are analogous to those occurring in a urine test introduced under the title "Ehrlich's diazo-reaction," which depends on the formation of a red azo-derivative by the reaction of the diazo-compound produced in the above manner with a substance occurring in urine in some diseases. The test is made by adding solutions of sodium nitrite and sulphanilic acid when, if the pathologic condition exists, the red is produced.

When the reaction is used for the detection of nitrites in water sulphanilic acid and amino-naphthalene are added in acid solution to a sample of the water. If nitrite is present the color is soon produced. No reaction occurs with nitrates. The test is very delicate; 1 part of nitrogen as nitrite in 1,000,000,000 parts of water can be easily detected, using only about 5 c.c. of the sample.

Phenylhydrazine hydrochloride.—This substance is now largely used as a test for sugars. It is a fawn-colored, crystalline powder with an odor recalling that of the geranium. It irritates the skin, producing in some persons an annoying eruption. It is liable to decomposition, becoming dark and pasty and of offensive odor. It should not be used in experiments or tests unless it is in good condition. It forms with ketonic and aldehydic bodies characteristic compounds, insoluble in water, termed "*osazones.*" The osazones are obtained in several ways. A common method is to heat the sample with phenylhydrazine compound and sodium acetate for some time in boiling water when the osazone separates.

Dextrose and levulose yield the same osazone, as molecules of the hydrazine group attach themselves to the two terminal carbon atoms, thus breaking up the aldehydic and ketonic structures which are, respectively, characteristic of the two compounds.

Lactose and maltose yield osazones; sucrose does not.

Alkaloids

The *natural bases* or *alkaloids* are so called because they possess the power of neutralizing acids with which they form distinct and crystallizable compounds. They may be divided into two classes: (1) *Non-volatile alkaloids* consisting of C, H, N and O. These are solids, usually crystallizable, sometimes possessing a definite melting point and often capable of sublimation, though generally with partial decomposition. (2) *Volatile alkaloids*, consisting of C, H and N. These are liquids capable of partial vaporization at ordinary temperatures, and usually having very high boiling points. The salts of the volatile alkaloids are non-volatile, crystallizable solids.

The *alkaloids* bear a close resemblance to the substitution amines, but they are more complex in constitution, especially as regards the presence of oxygen, which is not contained in the common substitution amines.

As regards the general properties of the non-volatile alkaloids, they are mostly but slightly soluble in water to which they impart an alkaline reaction, and usually freely soluble in alcohol.

Many alkaloids are bitter, acrid or pungent; most of them have decided physiologic properties and are the proximate principles upon which the medicinal activities of the plants containing them depend. A synopsis of the formulas, sources and characteristics of the principal alkaloids is given on pp. 196 and 197.

The alkaloids often produce characteristic color reactions with the inorganic acids and may be identified by the concurrence of several of these tests which, singly, are of little value.

Alkaloids differ from inorganic bases in forming salts by direct union with the acid, not by substituting the hydrogen. Thus, morphine forms with hydrochloric acid the compound $C_{17}H_{19}NO_3HCl$; it is, therefore, called morphine hydrochloride (sometimes hydrochlorate), not morphine chloride. This is due to the fact that the alkaloids are analogous to NH_3 rather than to NH_4, and the reaction between morphine and hydrochloric acid is similar to the reaction $NH_3 + HCl = NH_4Cl$, in which the hydrogen is not replaced.

Heroin, $C_{17}H_{17}(C_2H_3O_2)NO_3$, a derivative of morphine, is used as a substitute for it.

The classification of the alkaloids in a group based on the property of forming definite salts with acids brings together compounds of very different structure. Moreover, the basic power differs considerably in different members of the group. Strychnine, morphine and quinine, for instance, form stable and definite compounds. Caffeine is a weak base, many of its salts being easily decomposed.

Several essentially different types of molecular structure are exemplified in the alkaloids.

Amine Type.—Betaine is an example of this structure. Its sources and compositions are described under Ptomaines.

Pyridine Type.—Many alkaloids are of this type, containing either the simple pyridine ring or the duplicated (quinoline) ring. When either of these is present, the molecular structure is stable and the substance resists the action of many reagents.

Purin Type.—This is exemplified in caffeine and theobromine. The former is the characteristic alkaloid of tea, coffee, and maté, and is present in small amount in cacao; the latter is the principal alkaloid of cacao (chocolate).

Hydroxyl and hydrocarbon groups are often present. The latter can often be oxidized by mild oxidizing agents to carboxyl groups, thus converting the alkaloids into acids. Several alkaloids have been obtained synthetically.

IMPORTANT ALKALOIDS

Name	Empirical formula	Source	Description
Conine	$C_8H_{17}N$	Water hemlock (*Conium maculatum*).	Liquid; boiling point 167°.
Nicotine	$C_{10}H_{14}N_2$	Tobacco (*Nicatiana tabacum*).	Liquid; boiling point 247°.
Sparteine	$C_{15}H_{26}N_2$	Broom (*Spartium scoparium*).	Liquid; boiling point 287°.
Morphine	$C_{17}H_{19}NO_3$	Opium (*Papaver somniferum*).	Prismatic crystals soluble in about 5000 parts of water.
Codeine	$C_{18}H_{21}NO_3$		
Narcotine	$C_{22}H_{23}NO_7$		More freely soluble in water than other alkaloids.
Apomorphine	$C_{17}H_{17}NO_2$	By heating morphine with hydrochloric acid to 150°.	Is distinguished by being emetic instead of narcotic.
Quinine	$C_{20}H_{24}N_2O_2$	Bark of species of *Cinchona* (*Peruvian bark*).	Quinine and cinchonidine are levorotatory; cinchonine and quinidine are dextrorotatory.
Quinidine	$C_{20}H_{24}N_2O_2$		
Cinchonine	$C_{19}H_{22}N_2O$		
Cinchonidine	$C_{19}H_{22}N_2O$		
Atropine	$C_{17}H_{23}NO_3$	Belladonna (*Atropa belladonna*).	Used as a mydriatic.
Homatropine	$C_{16}H_{21}NO_3$	From atropine.	Preferred to atropine because the effect is not as lasting.
Hyoscyamine	$C_{17}H_{23}NO_3$	Henbane (*Hyoscyamus niger*).	
Strychnine	$C_{21}H_{22}N_2O_2$	Nux vomica (*Strychnos nux vomica*).	Powerfully toxic.
Brucine	$C_{23}H_{26}N_2O_4$		
Hydrastine	$C_{21}H_{21}NO_6$	Golden Seal (*Hydrastis canadensis*).	Used as an antiseptic.
Hydrastinine	$C_{11}H_{11}NO_2$	From Hydrastin.	A powerful oxytoxic.

Caffeine.....	$C_8H_{10}N_4O_2$	Tea, coffee, kola, maté.	Very feebly basic.
Cocaine.....	$C_{17}H_{21}NO_4$	Coca (*Erythroxylon coca*).	A local anesthetic.
Theobromine....	$C_7H_8N_4O_2$	Cacao (*Theobroma cacao*)	Resembles caffeine.
Aconitine.....	$C_{30}H_{47}NO_{11}$	Aconite (*Aconitum napellus*).	A powerful poison.
Veratrine.....	$C_{32}H_{49}NO_9$	Sadadilla (*Asagræa officinalis*).	Used locally in neuralgia; rarely internally.
Colchicine.....	$C_{22}H_{25}NO_6$	Colchicum (*Colchicum autumnale*)	
Pilocarpine.....	$C_{11}H_{16}N_2O_2$	Jaborandi (*Pilocarpus jaborandi*).	A powerful sialagogue and diaphoretic.
Pelletierine.....	$C_8H_{13}NO$	Pomegranate (*Punica granatum*).	A tenicide.
Physostigmine (Eserine).....	$C_{15}H_{21}N_3O_2$	Calabar bean (*Physostigma venenosum*).	A powerful myotic.
Gelsemine.....	$C_{24}H_{28}N_2O_4$	Yellow Jasmine (*Gelsemium sempervirens*).	
Emetine.....	$C_{30}H_{44}N_2O_4$(?)	Ipecac (*Cephaëlis ipecacuanha*).	
Sanguinarine....	$C_{20}H_{15}NO_4$	Bloodroot (*Sanguinaria canadensis*).	
Berberine.....	$C_{20}H_{17}NO_4$	*Hydrastis canadensis*.	

Basic nitrogenous bodies occur in, and are produced by, the decomposition of animal tissues. These are called *ptomaines* and are sometimes referred to, as the *cadaveric alkaloids*.

Many artificial compounds allied to the alkaloids have attained prominence in therapeutics during recent years. They are sometimes called the "coal-tar synthetics" in recognition of their origin.

Acetanilide, *Antifebrine*, $C_6H_5NH(C_2H_3O)$.—This is obtained by the reaction of aniline with acetic anhydride. It forms colorless and odorless crystals, soluble in 200 parts of cold water, much more freely in boiling water, alcohol, ether and chloroform. It is used as an antiseptic dressing and internally as an antipyretic.

Antipyrine, $C_{11}H_{12}N_2O$, forms colorless crystals, freely soluble in water, alcohol and chloroform.

Phenacetine, *acetphenetidine*, $C_6H_4(NHCH_3CO)OC_6H_5$, forms colorless crystals slightly soluble in cold water, alcohol, ether and chloroform.

Creatinine, $C_4H_7N_3O$. This is an ingredient of normal urine and of the juice of flesh. It is present in meat extracts. It is a strong base.

PTOMAINES

The chemical changes classed under the terms *fermentation* and *putrefaction* are caused by living organisms, mostly very minute, included under the general title "microbes." It seems probable that all such transformations are due to enzyms. The principal action is the breaking down of complex nitrogenous ingredients of the living tissues, often by hydrolysis, but also by other types of action, especially oxidation when the action occurs in the presence of air. It follows, therefore, that if air be excluded, the chemical changes will be somewhat different, and hence a distinction is made between the usual (aërobic) decompositions and those that occur out of contact with free oxygen (anaërobic).

The products of aërobic fermentation and putrefaction have been of late studied with great zeal. Many of them are distinctly basic, resembling the alkaloids. Furthermore, the normal processes of animals give rise to basic bodies. Care must be taken not to confuse the products of animal tissues with the products of microbes inhabiting the tissues, fluids or cavities of animals. The latter are ptomaines for they are the result of fermentation or putrefaction apart from the vital action of the animal. As such resulting bodies cause disease by absorption into the fluids of the animal they are sometimes termed "toxins."

Microörganisms either directly or by intermediate action of enzyms may produce alcohols, acids, neutral substances, cyclic compounds and nitrogenous derivatives; in fact, representatives of any class of organic compounds. The term ptomaine is derived from a Greek work meaning dead body.

It is to be noted that the ptomaines are not peculiar as a class among basic organic bodies, nor are they the only products of decompositions.

All ptomaines contain nitrogen, but the relation of this to the other atoms is dependent on the nature of the original molecule and the microbes or enzyms which bring about the transformation. Of the different types of combination that nitrogen may exhibit, amino-, azo- and diazo-groups are the most common. Pyridine compounds are not usual among the products of ordinary putrefaction; nitro- and nitroso-groupings are never observed.

The amines observed range in complexity from true basic monamins to tetramides with acid function.

Of the simpler type are some common ptomaines, such as *putrescine*, $(N_2H_4(CH_2)_4$, tetramethene diamine, and *cadaverine*, $(NH_2)(CH_2)_5$, pentamethenediamine.

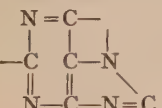
Choline.—Salts of this base occur in many animal and vegetable tissues. It was originally extracted from bile to which the name refers. Its gylcerophosphate exists in lecithins.

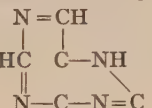
Neurine.—This is produced in some putrefactions.

Muscarine occurs associated with choline in poisonous mushroooms.

Betaine occurs in the sugar beet.

Purins.—Under these terms, the first being now much in vogue, is included a number of bodies of complex structure which it has been proposed to regard as derived from a hypothetical radical termed the "purin nucleus." From this, by association with other radicals, such as amidogen, imidogen, hydroxyl and carbonyl, formulas of the members of the series may be obtained. The following formulas show the relations of some of the members of the series to the purin nucleus and to purin itself:

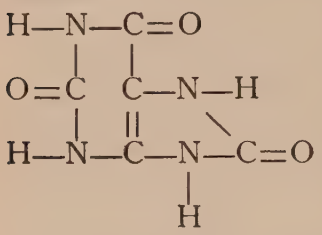

Purin nucleus


Purin

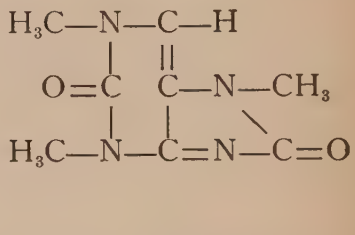
It will be seen that purin is, in a measure, a duplicated urea, the oxygen being absent and part of the hydrogen replaced by carbon. The purin

bodies are at present attracting much attention owing to their supposed relation to animal nutrition and metabolism. They exist in many foods and abundantly in tea, coffee, matè and cacao.

The relation between uric acid and caffeine is shown by the structural formulas.



Uric acid



Caffeine

Uric Acid, Trioxypurin, $C_5H_4N_4O_3$.—This occurs in small amount in the urine of mammals and abundantly in that of birds and reptiles. It can be obtained by strongly acidulating urine with hydrochloric acid and allowing the mixture to stand for some hours. Uric acid separates as a crystalline precipitate, usually brownish, from adherent coloring matter. When pure it is in colorless crystals, almost insoluble in cold water and only slightly soluble in boiling water. It forms several derivatives with sodium, potassium and ammonium, usually called "urates," which are more soluble in water than the acid itself. Uric acid does not contain the carboxyl radical, but the group HNCO, which occurs thrice in the molecule, confers nominal acidity.

Xanthin, Dioxypurin, $C_5H_4N_4O_2$.—This occurs in small amount in urine, but is more abundant in flesh juice, hence is found in commercial meat extract. It is colorless, crystalline and nearly insoluble in cold water.

Purin bodies are without nutritive value to the higher animals, hence any that are present in the food are passed off as promptly as possible by the excretions. The ordinary waste of tissue (destructive metabolism) in the animal produces purins, hence the excretions will contain both those in the food and those formed in the body. The former are termed "exogenous purins," the latter "endogenous purins."

PROTEINS

Proteins are complex bodies that form the essential portions of living tissues. They all contain carbon, hydrogen, oxygen and nitrogen; most

of them contain also sulphur; a few contain phosphorus, and a few contain iron. Even copper has been found in some, and it is not unlikely that elements, not usually existing in natural organic bodies, are present in proteins having highly specialized function or developed under exceptional conditions.

In structural formula proteins are all very complex, containing open and closed carbon chains. The nitrogen is probably partly in a pyridine ring and partly in a cyanogen or amine form. Some authorities distinguish between proteins and albuminoids, limiting the latter term to gelatin and closely analogous bodies. Other authorities limit the term protein to substances that yield amino-acids on decomposition by certain processes. These distinctions, however, cannot be regarded as final, and it is sufficient for present study to classify a considerable number of bodies under the general terms here used, even though appreciable differences in properties are noted. The proper classification will be made when the rational formulas become known.

Proteins are generally colorless or faintly yellow amorphous solids, soluble in water, but some require for this purpose the coincident presence of certain salts. Some dissolve in alcohol. Water solutions putrefy promptly, under ordinary conditions, but this is merely the result of the action of microbes. In the presence of antiseptics or in sterile solution proteins are practically permanent. They are ordinarily eminently colloidal, hence have very low diffusive power, but some have obtained crystalline, and there is no reason to doubt that all of them are capable of crystallizing under certain conditions. Solutions of proteins have levorotatory power.

A satisfactory classification of proteins is impossible in the present imperfect state of knowledge.

The following is a list of some important proteins.

Simple proteins or albumins:

Albumins proper: Ovalbumin, seralbumin, lactalbumin, vegetable albumins.

Globulins: Fibrinogen, vitellin, myosin, crystallin.

Nucleoalbumin: Casein.

Albuminates: Acid albuminate, alkali albuminate.

Albumoses.

Peptones.

Coagulated proteins: Fibrin, coagulated albumins.

Compound proteins:

Hemoglobins.

Glyco-proteins: Mucins, hyalogens, amyloid.

Nucleoproteins: Nucleohiston, cytoglobin.

Albuminoids: Keratin, elastin, collagen.

Proteins are precipitated from solution by many methods. When the precipitate cannot be dissolved without chemical change the action is termed "coagulation." Coagulation is brought about by heat in some cases, by chemical agents in others; each protein requiring particular methods. When quite dry, proteins show little tendency to change. By strong heating they are converted in a mixture of substances, among which pyridin and some of its derivatives are especially noticeable.

Coagulated Proteins.—Under this term are included proteins rendered insoluble in their normal solvents, pure water or saline solutions, as the case may be. In some cases they may be identical with the original body, but in most cases they are probably modified either by hydrolysis or oxidation with or without division into two or more new substances. Most of them can be converted into proteoses and finally into peptones by the action of some enzyms, and on this fact depends the digestibility of many articles in which by cooking the proteins are coagulated.

Albumins Proper.—This group includes *ovalbumin* (*egg albumin*), *seralbumin* (*blood albumin*) and *lactalbumin* (*milk albumin*). Care must be taken not to confuse "albumin" with "albumen." The latter term refers to the nutritive material surrounding an embryo. It contains one or more proteins which may or may not be albumins. White of egg is the "albumen" of the egg. It contains ovalbumin, water and other bodies. The seeds of many plants contain a large amount of material around the embryo. This is called the "albumen" of the seed. In the common cereals this albumen contains several proteins, with much starch and some fatty matter and salts.

The albumins are soluble in water and in weak saline solutions. In strong saline solution they are coagulated at a temperature of about 60°. Alkalies and very small amounts of acids do not precipitate them, but larger amounts do, as also many neutral salts, among which are ammonium sulphate and mercuric chloride.

Globulins.—Globulins are insoluble in water, but soluble in dilute solutions of sodium chloride. They are precipitated unchanged from these solutions by dilution with pure water.

Vitellin is obtained from egg-yolk, it resembles somewhat the nucleo-albumins. It has not been obtaineed free from lecithin.

Crystallin is obtained from the crystalline lens.

Fibrinogen.—This exists in blood plasma When blood clots, the fibrinogen is converted into fibrin, which forms the clot and encloses the blood corpuscles. This coagulation occurs under the influence of another substance, termed "fibrin-ferment," or "thrombin" which also exists in the blood plasma. The nature of thrombin is not known, but it is probably an enzym.

Myosin is obtained from muscles. According to some authorities, the fluids in living muscles contain a protein termed myosinogen which is converted after the death of the tissue, when the stiffening (*rigor mortis*) sets in, into myosin.

Nucleoalbumins.—These are distinguished from most other proteins by containing notable amounts of phosphorus. The most important is casein, the principal portion of the fresh curd of cow's milk. In fresh milk the casein exists in association with some calcium phosphate and is probably partly in a jelly-like condition, not in true solution. Most acids, many mineral salts, and several enzyms coagulate milk, but much protein remains in solution, and it is probable that hydrolysis occurs, and the original proteins are split into several substances some of which precipitate and others remain dissolved. A solution of mercuric nitrate in excess of nitric acid precipitates all the proteins of cow's milk.

Cheese is protein matter obtained from milk either by the action of acids or by rennet, a preparation of enzyms from the stomach of the calf. The acid usually employed is lactic, the result of the natural souring of milk by fermentation of milk sugar. Cheese, even when fresh, does not contain the same proteins as milk, and in ripe cheese further changes have occurred through the action of microbes and enzyms, by which amino-compounds have been produced. Ammonium compounds are present in well-ripened cheese. Sometimes ptomaines, either amine derivatives or azo-compounds are present, thus making the cheese poisonous.

Acid-albuminates and Alkali-albuminates.—Many proteins combine to a limited extent with acids or with alkalies, producing compounds that have characteristic properties. By the action of somewhat strong solutions of alkali on natural proteins, cemical changes are produced in the latter, among which are the elimination of nitrogen and sulphur. By dissolving proteins in hydrochloric acid, acid-albuminates may be obtained.

Both these products have certain properties in common. They are nearly insoluble in water and dilute solution of sodium chloride, but are dissolved by water on the addition of a little acid or alkali. The solution is not coagulated by heat, but can be precipitated without heat by neutralizing the solvent substance, that is, adding acid to the alkali-albumin and alkali to the acid-albumin. Strong mineral acids precipitate both classes of albuminates.

Albumoses and Peptones.—The action of hydrolyzing enzyms, such as those in the gastric juice and pancreatic secretions on proteins, results finally in the formation of a substance or mixture of substances, similar to the common proteins in many ways but much more diffusible and much less coagulable. This is called *peptone.* In the course of its formation from the original protein, several intermediate transformations occur, the products of which are, collectively, called *proteoses* or *albumoses.* These products differ with the conditions of action and the protein and enzym.

Hemoglobin.—This is the coloring matter of blood corpuscles. It is distinguished from many other proteins by containing iron, which is part of the molecule and not, as with some proteins, merely due to adherent mineral matter. Chlorophyl, the green coloring matter of plants is associgted with iron, and its functions are somewhat analogous to those of hemoalobin. In some animals the iron in hemoglobin is partly or wholly replaced by copper.

Hemoglobin is very soluble in water, producing a red solution that shows characteristic absorption bands. Its principal property is the power to take up oxygen and to give this up again under the influence of different substances. The oxygen compound differs slightly in composition according to the pressure of the gas from which the absorptiont akes place. As a rule, hemoglobin absorbs only free oxygen. It has affinity for other bodies, such as nitrous oxide, nitric oxide, hydrogen sulphide, carbon monoxide, carbon dioxide and acetylene. The affinity for carbon monoxide and nitric oxide is stronger than the affinity for many other substances. All these derivatives of hemogoblin give characteristic absorption bands. By exposing oxyhemoglobin for some time to the action of free oxygen or to mild oxidizing agents, a substance known as *methemoglobin* is formed.

Mucin.—Under this term several proteins are included. They are found in the secretion of mucous membranes, in connective tissue, tendod and the submaxillary gland. Protein matter that coagulates with nitric acid, frequently appears in urine. It is also termed mucin, but many

authorities regard it as essentially different from true mucin, and properly a nucleoalbumin. True mucin may, however, be present in urine containing a large amount of mucus. By the action of acids, mucin can be hydrolyzed and a reducing carbohydrate formed.

NUCLEINS.—These are a series of bodies containing notable amounts of phosphorus. They are widely distributed in the vegetable and animal kingdom, and have been classified in two groups: Nucleins proper, which yield proteins, phosphoric acid and xanthin bases; and pseudonucleins that yield no xanthin bases. The true nucleins are obtained as insoluble residues in the digestion of nucleoproteins by gastric juice. By the action of alkalies, nucleates are formed, from which nucleic acids may be obtained. All nucleins, by boiling with dilute acids, yield a series of nitrogenous bodies termed the *xanthin* or *nuclein bases*. They have closed structural relations to some alkaloids, leucomaines and uric acid. It has been suggested that they are all derived from a body having the formula $C_5H_4N_4$ to which the name *purin* has been applied. Hence the group is often called the "purin bases." (See Purins.)

KERATIN is the chief protein constituent of horny structures, hair and nails. Some of its reactions are similar to those of the proteins proper, but it is not digested by gastric or pancreatic secretions.

ELASTIN occurs in connective tissue, especially the cervical ligament. It is insoluble in water, and dissolves only slowly in alkalies and acids.

COLLAGEN is the material in connective tissue and bone from which gelatin is obtained. GELATIN is prepared by boiling the tissue with water. The process is very slow at ordinary pressure, but in a closed vessel, the temperature can be raised considerably and the gelatin rapidly produced. The change is doubtless a hydrolysis.

The food material called *isinglass* is probably a collagen that is easily converted into gelatin. Ordinary gelatin dissolves in hot water, and the solution on cooling sets to a jelly if considerable of the gelatin is present. Solutions of gelatin are promptly precipitated by common tannins. The tanning of skins is dependent on the reaction by which the proteins are rendered insoluble and non-putrescent. This was originally carried out by the use of tannins, but several other methods are now in use. Formaldehyde converts gelatin into a mass insoluble in water.

VEGETABLE PROTEINS.—As a purely vegetable diet will support life satisfactorily for a long period, it is reasonable to suppose that the vegetable proteins are of the same general character as those of animal origin, but the isolation and classification of the former are as yet very incomplete.

Investigations have been made into the proteins of important cereals. The principal proteins of wheat flour are *gliadin* and *glutenin*. The former, which constitutes nearly half the protein matter of the grain, is soluble in pure water and in dilute alcohol, but almost insoluble in water containing the mineral matters of the wheat grain. Glutenin is insoluble in water, dilute saline solutions and dilute alcohol. The glutinous property of wheat flour is due to both the proteins, the gliadin giving the adhesiveness and glutenin the solidity.

Lecithins.—These are complex bodies that occur in the protoplasm of many forms of cells, either alone or in combination, or close association, with proteins. A lecithin is an ester derived from glycerophosphoric acid by substitution of two of the hydrogen atoms of the latter by two molecules of radicals of the fatty acids and the other hydrogen atom by a base "*choline*."

Enzyms

Enzyms are nitrogenous bodies belonging to the group of *catalysts* (see p. 21) analogous in composition and general properties to ordinary proteins, but are distinguished by power to bring about transformations without being themselves permanently affected. Nothing is known as to their empirical formulas; in fact, they have not been prepared in a perfectly pure condition. They are usually amorphous, colorless or slightly yellow, soluble in water, but not appreciably in other solvents. The solution in water soon putrefies. Some enzyms are affected injuriously by light, and all of them lose their characteristic functions when heated, resisting, however, this treatment better when dry than in solution. Many substances restrain the action of enzyms; some of these, such as salicylic acid, boric acid and benzoic acid are largely used for controlling or preventing their action. Enzyms are often termed "*non-organized ferments*," ordinary microbes being designated "*organized ferments*."

Each enzym has its peculiar "optimum" condition, under which it is most active. Conditions that favor one enzym often restrain or interrupt the action of others. Thus, pepsin, the principal enzym of gastric juice, is favored by the presence of a small amount of hydrochloric acid, but restrained by a larger amount. Trypsin the corresponding enzym of the pancreatic secretion, is favored by the presence of a feebly alkaline body.

The manner of action of enzyms is not known. It has been suggested that they combine temporarily with the substances involved in the reaction and are set free unchanged when new molecules are formed. Thus,

the hydrolysis of sucrose by invertase would consist in, first, a combination of sucrose molecules and water, one to one, with a molecule of the enzym; then, an intermingling of the water molecule and sucrose molecule to the exclusion of the enzym, which is thus liberated. The molecule formed by the intermingling of the water and carbohydrate is immediately broken into dextrose and levulose. The enzym is free to repeat its action. In theory, therefore, it is inexhaustible; in practice, the accumulation of products and the constantly increasing dilution interfere with and ultimately suspend the action. It has been found experimentally that invertase can hydrolyze 100,000 times its weight of sucrose and still be active.

Enzyms may be regarded as the connecting link between living and nonliving matter. They have some of the characteristics of each class, but they have, as far as known no power of reproduction.

The following are some important enzyms, with their source and characteristic actions.

Diastase.—From malt. Converts starch into maltose and dextrin by hydrolysis. Favored by mild alkalinity of solution and restrained by acidity and by salicylic acid.

Takadiastase (Japanese, *taka*, strong).—From a fungus that grows on bran. Similar to diastase in its action.

Amylopsin.—From pancreatic secretion similar to diastase.

Invertase.—From yeast, hydrolyses sucrose to a mixture of equal parts of dextrose and levulose (invert sugar). Favored by slight acidity.

Synaptase.—From tissues, especially seeds, of plants of the order Rosaceæ. It converts amygdalin by hydrolysis into benzaldehyde, dextrose and hydrogen cyanide.

Myrosin (*myrosase*).—Exists in white and black mustard. It hydrolyses sinalbin in the former and sinigrin in the latter, producing the irritating materials upon which the local action of mustard depends.

Pepsin.—The principal enzym of gastric juice. It hydrolyses proteins to proteoses and finally to peptones, but the peptonizing action is slow and often incomplete. Pepsin is most active in the presence of a small amount of hydrochloric acid.

Trypsin.—One of the enzyms of the pancreatic secretion. It hydrolyzes proteins to proteoses and then to peptones, being more rapid than pepsin. It acts best in feebly alkaline solution. By prolonged action peptones are hydrolyzed to leucin and tyrosin.

Ptyalin.—This is the characteristic enzym of saliva. It hydrolyzes starch to maltose and dextrin, and sucrose to dextrose and levulose.

Steapsin.—An enzym of the pancreatic secretion. It hydrolyzes fats to glycerol and free acids.

A similar enzym exists in the castor bean.

The juice of the papaw (*Carica papaya*) contains enzyms capable of digesting proteins and starch. The juice of the pineapple contains an enzym that digests proteins.

Catalase.—An oxidizing enzym obtained from fresh leaf tobacco, but probably widely distributed. It decomposes hydrogen dioxide.

Rennin is found in gastric juice, especially in that of the fourth stomach of the calf. Its characteristic action is the coagulation of milk which is due to a hydrolytic change in the casein, by which this is split into several proteins some of which precipitate and others remain in solution. The precipitate and liquid are termed, respectively, "curds" and "whey." Rennin in solution is rendered inactive by exposure to a temperature of 60° to 70° which is somewhat lower than that required for most enzyms.

Milk contains several enzyms that have digestive and limited oxidizing powers, but they have not been satisfactorily isolated.

The terms proteolytic (protein hydrolyzing), amylolytic (starch hydrolyzing) and lipolytic (fat hydrolyzing) are used in connection with enzyms.

CLINICAL CHEMISTRY

This term covers the application of analytic chemistry to diagnosis, especially the testing of secretions and excretions. In this book will be given an outline of the testing of milk, stomach contents and urine and blood.

MILK

Milk consists principally of water, holding minute globules of fat in suspension, and a carbohydrate, proteins and mineral matters in solution. The proteins may be partly in a jelly-like condition. Cow's milk and human milk are the most important. The following table is an approximate statement of the composition of each, but many samples of normal milk will differ somewhat from these figures. The figures are per cent.; the remainder is water:—

	Cow's milk	Human milk
Fat	4.0	3.5
Proteins	3.5	6.5
Sugar	4.5	1.5
Mineral matter	0.75	0.25
	12.75	11.75

The sugar is termed "lactose." The proteins consist principally of casein, with some albumin and small amount of globulin.

By the action of rennet or by acids the proteins are partly coagulated, and the precipitate entangles the fat. The nearly clear liquid is termed *whey*. It contains a notable amount of proteins. The precipitated matter is termed *curd* and becomes *cheese*. When milk stands the fat accumulates in the upper layer forming *cream*.

The United States government, acting under authority of the Federal Food Law, has established the following official standards.

Milk is the whole, fresh, clean, lacteal secretion obtained by the complete milking of one or more healthy cows, properly fed and kept, excluding that obtained within fifteen days before and five days after calving, or such longer period as may be necessary to render the milk practically colostrum free.

Pasteurized milk is milk that has been subjected to a temperature not lower than 145° F. for not less than thirty minutes, after which it is promptly cooled 50° F., or lower.

Milk is usually tested for fat, total solids and preservatives.

There is a definite relation between the fat, total solids and specific gravity of milk, and if any two of these are known, the third can be calculated. If the fat is deducted from the total solids, the remainder is *solids-not-fat*. Thus, in the analyses given above—

	Cow's milk	Human milk
Total solids	12.75	11.75
Fat	4.00	3.5
Solids-not-fat	8.75	8.25

In normal cow's milk, the solids-not-fat usually do not go below 8.5%. A lower figure suggests watering. A percentage of fat below 3.5 suggests skimming.

Total solids of milk are taken by evaporating a known amount in a flat basin, at the boiling point of water. Good approximations may be made by running 2 c.c. into one of the shallow dishes used for bacteria culture (Petri dishes), heating this on the water-bath for several hours, cooling, weighing and deducting the weight of the dish.

Specific Gravity.—This is best taken with a special hydrometer called a *lactometer*. The normal temperature is 60° F. (15.5° C.). If the milk is not at this temperature correction must be made by a special table.

Fat.—The exact determination of fat is a different operation, but determinations quiet sufficient for ordinary purposes can be made by the Leffmann-Beam method, as follows:

The distinctive feature is the use of fusel oil, the effect of which is to produce a greater difference in surface tension between the fat and the liquid in which it is suspended, and thus promote its readier separation. This effect has been found to be heightened by the presence of a small amount of hydrochloric acid.

The test-bottles have a capacity of about 30 c.c. and are provided with a graduated neck, each division of which represents 0.1% by weight of butter fat.

15 c.c. of the milk are measured into the bottle, 3 c.c. of a mixture of equal parts of amyl alcohol and strong hydrochloric acid added, mixed, the bottle filled nearly to the neck with concentrated sulphuric acid, and

the liquids mixed by holding the bottle by the neck and giving it a gyratory motion. The neck is now filled to about the zero point with a mixture of sulphuric acid and water prepared at the time. It is then placed in the centrifugal machine, which is so arranged that when at rest the bottles are in a vertical position. If only one test is to be made, the equilibrium of the machine is maintained by means of a test-bottle, or bottles, filled with a mixture of equal parts of sulphric acid and water. After rotation for from one to two minutes, the fat will collect in the neck of the bottle and the percentage may be read off. It is convenient to use a pair of dividers in making the reading. The legs of these are placed at the upper and lower limits respectively of the fat, allowance being made for the meniscus; one leg is then placed at the zero point and the reading made with the other.

Cream is to be diluted to exactly ten times its volume, the specific gravity taken, and the liquid treated as a milk. Since in the graduation of the test-bottles a specific gravity of 1.030 is assumed, the reading must be increased in proportion.

A more accurate result may be obtained by weighing in the test-bottle about 2 c.c. of the cream and diluting to about 15 c.c. The reading obtained is to be multiplied by 15.45 and divided by the weight in grams of cream taken.

The mixture of fusel oil and hydrochloric acid seems to become less satisfactory when long kept. It should be clear and not very dark in color. It is best kept in a bottle provided with a pipet which can be filled to the mark by dipping. Rigid accuracy in the measurement is not needed.

Distinctions between Raw and Boiled Milk.—Boiled milk is less nutritious than raw milk. Even pasteurization injures to a slight extent the nutritious value. Tests for determining if milk has been heated to or near to the boiling temperature are available. The best is the *Benzidine Test.* A solution of the commercial benzidine hydrochloride (about 10 %) serves well. A small amount of this should be added to the sample and then a small amount of hydrogen peroxide Raw milk gives promptly a distinctly blue liquid; pasteurized milk shows a moderate color, but boiled milk undergoes no change.

Preservatives.—The preservatives likely to be used in milk are boric acid, borax and formaldehyde.

Borax and boric acid are detected by the following method: A few drops of the sample are placed in a watch-glass or porcelain basin, a drop of strong hydrochloric acid and of strong tincture of turmeric added, the

mixture evaporated to dryness on the water-bath, cooled and treated with ammonium hydroxide. In the presence of boric acid or borax a bluish-green is produced. Pure milk will give a brown.

Formaldehyde.—The following test, originally proposed by Bonnet, is due to the vapor of formaldehyde, and avoids the fallacies of some of the older tests. A solution is made by dissolving 0.035 gram pure morphine sulphate in 10 c.c. of sulphuric acid. This solution does not keep well. A convenient amount of the milk is placed in a dish or beaker, a watch-glass containing 1 c.c. of the above solution is floated on it, and the dish covered with a glass plate. The materials are allowed to remain undisturbed at room-temperature for several hours. Formaldehyde is indicated by the development of a color ranging from pink to dark blue. A black discoloration is disregarded. Bonnet found that with 1 part of formaldehyde to 25,000 parts of sample a distinct color appeared in one hour.

STOMACH CONTENTS (CHEMICAL EXAMINATION)

Gastric juice is the digestive secretion of the stomach. In the normal condition its principal ingredients are the enzyme pepsin, and gastric rennin, and hydrochloric acid (about 0.2%). The secretion of gastric juice follows psychic stimulation as well as from the drinking of liquids and the eating of solid foods.

Before making an analysis of the stomach contents the gastric residum is removed and a test meal given to stimulate the gastric cells. At fifteen minute intervals by means of the Rehfuss Gastric Tube samples of the stomach contents are obtained, until the stomach is empty.

QUALITATIVE

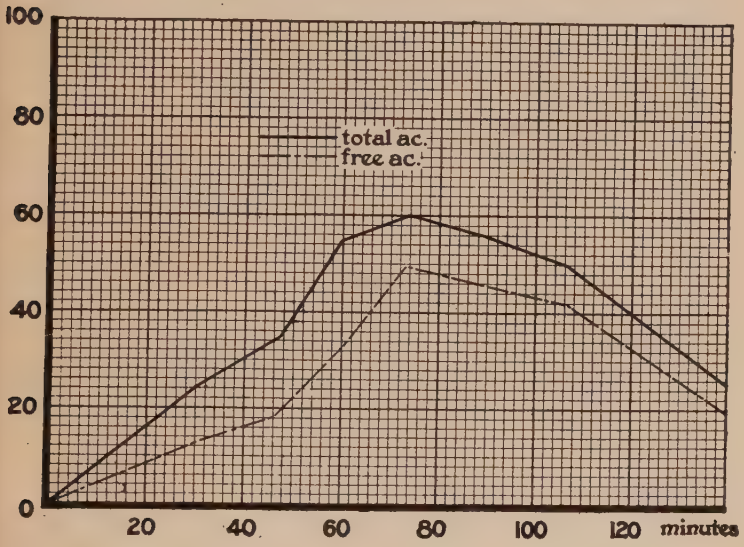
Acidity.—The hydrochloric acid may exist as such or be united with the proteins present in the stomach at mealtime. This state is often termed "combined" hydrochloric acid, but this is misleading; the term "bound acid" is preferable. Litmus paper is reddened by all the acids and acid salts that may occur in gastric juice. Ordinarily the indicator used is phenolphthalein which reacts with mineral acid, organic acid, combined acid and acid salts and thus the total acidity is obtained.

Special Tests.—Several tests for distinguishing the nature of the acid are in common use.

Günzberg's Test is most satisfactory for free HCl. Dissolve 2 grams of phloroglucinol and 1 gram of vanillin in 100 c.c. of 95% ethyl alcohol. Place 1–2 drops of this reagent in a small evaporating

dish and evaporate carefully to dryness. Place a glass rod in the mixture to be tested and draw the moist end through the dried reagent. Warm gently and note the formation of a purplish-red when HCl is present.

Uffelmann's Test for Lactic Acid. (Uffelmann's reagent is prepared by adding ferric chloride solution to a 1% solution of phenol until an amethyst-blue color is obtained, due in part to the formation of a ferric salt of phenol and in part to the reduction of some of the iron.)



Acidity Curves of Normal Human Stomach. (*Hawk.*)

To 5 c.c. of Uffelmann's reagent placed in a test tube, add an equal volume of strained gastric juice. A canary yellow or greenish yellow develops if lactic acid is present even to the extent of 0.01%.

QUANTITATIVE ANALYSIS

Total Acidity.—Measure 1 c.c. of strained stomach contents into a small evaporating dish. Dilute with distilled water. Add 2 drops of a 1% alcoholic solution of phenolphthalein and titrate with N/100 sodium

hydroxide until a faint pink color is obtained and persists for about two minutes. Take the burette reading and calculate the total acidity.

Calculation.—Note the number of cubic centimeters of N/100 NaOH required to neutralize 1 c.c. of stomach contents, and multiply it by 10 to obtain the number of c.c. N/10 NaOH necessary to neutralize 100 c.c. of stomach contents. This is the method of calculation most widely used.

Free Acidity.—Measure 1 c.c. of strained stomach contents into a small evaporating dish. Dilute with distilled water. Add 1–2 drops of Töpfer's reagent (one-half gram di-methyl-amino-azobenzene dissolved in 100 c.c. of 95% alcohol) and titrate with N/100 NaOH until the initial red color is replaced by orange yellow. Calculate as in total acidity.

The normal gastric residuum has an average total acidity of 30 and an average free acidity of 18.5.

The height of the normal gastric curve is generally reached in one or two hours depending on the kind of meal taken and the motor activity of the stomach. The graph, p. 213 (from Hawk's "Practical Physiological Chemistry") shows the acidity curves of the normal stomach.

URINE

Normal urine is a clear, pale yellow or amber-colored fluid of acid reaction. Its specific gravity within the limits of health may vary from 1.010 to 1.030. The quantity passed in the twenty-four hours by a male adult in good health may be approximately fixed at 50 fluidounces—about 1500 c.c. The total solid matter is about 4%, that is, 100 c.c. of urine will leave on evaporation to dryness about 4 grams of residue, a little more than half of which is organic matter.

Composition of Normal Urine

(From data published by Folin. Male, weighing about 130 pounds on liberal protein diet)

Volume in 24 hours	1239 c.c.
Urea	34.7 grams
Creatinine	1.58 grams
Uric acid	0.44 grams
Chlorine	6.10 grams
Phosphates (as P_2O_5)	4.50 grams
Sulphates (as SO_3)	
Inorganic	3.25
Ethereal	0.25
Acidity (decinormal acid) for total volume	651.0 c.c.

The composition of urine is very complex, and the many published analyses are unsatisfactory. It is convenient to divide the solid matters into two groups, organic and inorganic. The most important of the former group are urea and uric acid. Urea is excreted in considerable amount (30 to 40 grams per day in the case of a healthy male adult), but varies with the protein intake. The excretion of uric acid is less than 1 gram. The inorganic ingredients consist of sulphates, chlorides and phosphates, potassium, sodium, calcium and magnesium being the positives present; but it is not possible to state just how these combinations occur. Most of the chlorine occurs as sodium chloride. Calcium and magnesium probably occur as phosphates. Some esters, especially potassium phenyl-sulphate (see p. 170), occur in small amount. These are often termed "ethereal sulphates." Among the organic bodies often present in minute amount are acetone, aceto-acetic acid, indican and hippuric acid. In addition to these ingredients many others are present in very minute amounts.

Urea (see p. 189).—This is the most abundant solid ingredient of the urine, except in certain diseased conditions. In complete suppression of urine-excretion it accumulates in the blood. It does not decompose readily in pure solution, but in urine soon undergoes hydrolysis into ammonium carbonate under the influence of microorganisms. The reaction may also be brought about some enzyms, notably "urease" extracted from the jack bean.

$$CH_4N_2O + 2H_2O \rightarrow (NH_4)_2CO_3$$

Uric acid is described on p. 200.

Xanthin is present in very small amount in normal urine, but sometimes occurs in sufficient amount to form a calculus.

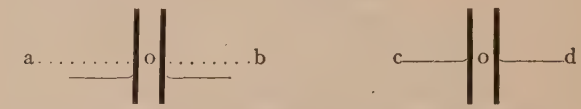
Specific gravity is generally taken by means of a urinometer, which is a graduated bulb-tube weighted so as to float upright. Extreme accuracy is not required, a difference of a few degrees not signifying anything clinically. In using the urinometer the following precautions are necessary:—

(*a*) The urine must be at a temperature near 60° F. (15.5° C.); the determination should not be made when the liquid is first passed.

(*b*) The instrument must be placed in carefully, and the glass vessel must be wide enough to allow it to float freely.

In reading the degrees care should be taken to avoid error from the curved line which the liquid forms with the stem. Some urinometers are graduated to read at the highest point of this curve, others at the actual

level of the liquid. To determine the proper method the instrument should be carefully floated in some distilled or rain water at a temperature of 60° and the position of the zero noted.



If the zero corresponds to the line a b each reading of gravity should be at the top of the curve, but if it corresponds to the position c d, then the reading should be along the real level of the liquid, and the eye should be placed on a line just below this level. If the zero point is at neither of the places noted the instrument is unsuitable for use.

The cheaper forms of urinometers are usually quite sufficient for clinical purposes.

Reaction.—Urine, when fresh, is generally decidedly acid, due probably, to acid sodium phosphate, but when uric is in excess it may contribute to the acidity. The acid reaction increases slightly after the urine has been passed, but very soon the mucus begins to decompose and causes the urea to become ammonium carbonate. The liquid becomes alkaline and foul. A neutral condition or transient alkalinity, called the *alkaline tide*, is seen in the urine secreted just after a meal, and an alkalinity due to decomposition is noticed in those cases in which, owing to obstruction, the liquid is retained in the bladder for some time.

For determining reaction, the so-called *neutral litmus paper* is suitable. A solution of litmus is prepared by boiling it in water; this is divided into two parts, to one of which some strong acid is added, drop by drop, until the color is wine-red. This is then mixed with the other half of the liquid. Slips of filtering paper are dipped in this liquid and dried. They will assume a purple tint and are very delicate, responding either to a trace of free acid or of alkali. By employing this form of paper we avoid the necessity of using two colors. The paper should be cut into pieces about one-half an inch square, one of these being dipped into the sample to be tested. No piece should be used a second time. Litmus *paper* is best kept in a closed bottle away from the light, but litmus *solution* must be kept in an open bottle. It will then keep for a long time, but in a closed bottle will soon decompose.

Abnormal Coloring Matters.—These include various modifications of the blood-coloring matters, biliary products and colors due to articles of food and especially drugs.

Blood Colors.—These give to the urine a smoky color when in small amount; large quantities color it red.

When blood itself appears in urine the corpuscles may be recognized by the microscope, and the condition is called *hematuria* provided the urine is acid, but if only the coloring matters of the blood are present the condition is called *hematinuria*. In the latter case the abnormal ingredients are recognized by spectroscopic and chemical methods. One of the most widely used tests for blood in urine is the Benzidine reaction. Centrifuge the urine, and pour off the supernatant portion. Place the residue (only a few drops) on a glass slide. Then add a drop or two of a saturated solution of benzidine in alcohol or glacial acetic acid and a few drops of fresh hydrogen peroxide and immediately a blue color will appear if blood is present. Be sure that this mixture is acid, if not add a drop or two of acid. A control test should be made substituting water for urine. It is important to remember that we may have a hematuria and yet be unable to see any red cells under the microscope, providing the urine is alkaline. Red cells disintegrate in an alkaline medium.

Bile acids (Mylius' test).—To about 5 c.c. of the sample add 3 drops of a 1:1000 aqueous solution of furfural. Incline the tube and carefully run down the side 2 to 3 c.c. of concentrated sulphuric acid, and note if any red ring appears (positive reaction) on shaking the mixture the entire liquid become red. A more delicate test is to filter an ounce of the urine and when the filter paper has dried distribute a few drops of nitric acid on the filter paper and if bile pigment is present there will be produced a play of colors.

Chlorides are diminished during febrile conditions, sometimes entirely absent. The amount in health depends largely on the diet and, of course, on the extent to which salt is used. 12 to 15 grams per 24 hours may be excreted on a rich diet and 2 to 3 grams on a low one. Chlorides are recognized by adding a small amount of nitric acid to the sample and then solution of silver nitrate. A white precipitate of silver chloride is formed.

Sulphates.—SO_4 occurs in urine in two forms of combination; ordinary sulphate, and as esters, especially potassium phenyl sulphate, $KC_6H_5SO_4$. This must not be confounded with potassium phenolsulphonate, $C_6H_4(HO)KSO_3$ (see p. 170).

Ordinary sulphates are detected by adding solution of barium chloride and a few drops of hydrochloric acid to the filtered urine. A white precipitate (barium sulphate) shows sulphates. The sulphuric ester does not respond to this test. By boiling the urine with hydrochloric acid this is

hydrolyzed and will then give the barium reaction. This method is utilized for determining the amount present. From the difference in weight between the barium sulphate produced from equal volumes of the sample with and without treatment with hydrochloric acid, the proportion of SO_4 present as ester may be calculated.

Phosphates.—Potassium and sodium phosphates are called alkaline phosphates; calcium and magnesium phosphates are called earthy phosphates. The former are freely soluble in water, but not all of the latter; both are soluble in acids.

The amount held in solution depends in part on the amount of acid, also on the temperature. These facts are important, because a deposit of phosphates may occur, either from alkalinity or deficient acidity of the urine, or from actual excess of the phosphates themselves. The clinical significance of these conditions is, of course, very different. By means of litmus, as already given, the reaction of the liquid can be easily ascertained. Deposits of phosphates are generally bulky and white, remaining undissolved when the liquid is boiled—being thus distinguished from urates—but dissolving in hydrochloric or nitric acid. Such deposits have no significance when found in urine which has become stale and has thus acquired an alkaline reaction.

Urine almost always produces a precipitate of earthy phosphate on boiling.

On adding a few drops of any strong acid the phosphate passes into solution. By this means the precipitate may usually be distinguished from proteins.

Phosphates are found as deposits in various forms, which are, in the main, distinguishable from each other and everything else by the microscope.

Oxalates.—Calcium oxalate, CaC_2O_4, is the only one requiring notice. It is deposited in the minute but very distinct octahedral crystals and also in dumb-bell forms.

Uric Acid.—Excess of uric acid sometimes produces a brick-red deposit of small crystals. Under the microscope, even with a low power—40 to 60 diameters—these show various forms, generally lozenge-shaped.

A deposit of urates may be recognized by the red color, and by dissolving in whole or in part by heating the liquid in which it is suspended.

Uric acid, or any of its compounds, may be recognized by the so-called *murexid test*. The sediment is treated on a watch-glass or cover

of a porcelain crucible, with a drop or two of nitric acid—not very strong—and then carefully evaporated to dryness. A drop of ammonium hydroxide is then added, and if uric acid is present a purple color will be produced. Caffeine also responds to this test.

Albumin.—The tests for albumin are dependent on its coagulation. The liquid should be filtered before the tests are applied and its reaction noted.

Heat.—The most delicate clinical test is the simple one by heat, adding acetic acid beforehand, only if the specimen be but faintly acid, and then boiling the *upper stratum* in a long, narrow test-tube, subsequently comparing the upper and lower strata with the aid of a dark background. Should a cloud form, a few drops of a dilute solution of acetic acid should be added. No dependence is to be placed on a cloud appearing some time after the urine has cooled, if acetic acid has been added in any save the smallest amount except with the rather rare Bence-Jones' protein with which the cloud disappears on heating. In the other event, the cloud is probably due to nucleo-albumin. The boiling test so used is very much more delicate than the nitric acid method. There is no test for serum-albumin without some source of fallacy. If much nucleo-albumin be present, and an excess of earthy phosphates, the heat test may mislead. Nucleoalbumin can usually be excluded by the use of citric acid, by the underlying method, applied to the cold urine.

Nitric Acid, Heller's Test.—This acid produces coagulation in the cold, and gives a method but little liable to fallacy. About 15 drops of commercial nitric acid are placed in a somewhat narrow test-tube, and about a dram of urine poured slowly down upon it, holding the tube considerably inclined. Another method, and one preferred by many, is to put the urine in first and pour the acid down the side of the inclined tube, when it will run below the urine and form a clear layer at the bottom of the tube.

Fallacies.—Urine rich in urea sometimes gives a precipitate of urea nitrate, which might be mistaken for albumin. It can be distinguished by its solubility when warmed, and by its crystalline character.

Excess of urates may also produce a misleading precipitation, but the ring produced by these is generally more irregular, and after a few hours is converted into the crystalline uric acid, which is easily recognized under the microscope.

In exceptional cases resinous bodies which have been given as medicines may be found in the urine in combination with the bases present. Such

compounds may be decomposed by the acid and the resin precipitated as an amorphous mass, which may simulate albumin. The distinction will be the odor of these resins and their solubility in strong alcohol. In addition to these points, the fact of their being administered will suggest precaution in regard to the test.

Nucleo-albumin.—This body, commonly called *mucin*, is usually present in urine and simulates albumin in some of the tests. Its clinical chemistry has been fully discussed by Dr. D. D. Stewart, who employed a commercial nucleo-albumin obtained from bile and believed to be identical with that occurring in urine. He found that solutions of citric acid both dilute and concentrated used by the underlaying method, as described in connection with the nitric acid test for albumin, gave distinct contact rings. Picric acid associated with citric acid also gave such precipitates, but picric acid alone gave with solutions containing not more than 0.02%. of nucleo-albumin only a tardily appearing haze.

Pus.—Pus is detected by the microscope, by which its cells may be seen in abundance; the liquid itself will give reactions for albumin. If a solution of caustic soda be added to urine containing an abundance of pus, and the mixture poured a few times from one test to another, it will become very thick and viscid.

Sugars.—*Dextrose* is the usual form. It may occur in minute amount in normal urine. Lactose, levulose and some oxidized derivatives of the carbohydrates occasionally occur. The ordinary clinical testing applies only to dextrose, which is often termed "glucose."

Glucose.—Reducing substances are normally present in urine to the extent of less than 0.2,% usually less than 0.1% for a 24 hour specimen. Folin and Berglund claim that glucose is excreted only when the kidney "threshold" for sugar is passed.

Benedicts's qualitative test is generally considered the most satisfactory test as it is less liable to give false positives and is much more delicate than Fehlings.

To about 5 c.c. Benedict's reagent in a test tube, add a pebble or two to prevent bumping and 8–10 drops of urine and mix. Boil vigorously and carefully for 1–2 minutes and allow to cool. A general turbidity, yellow or red, the color depending on the size of the crystals of reduced copper as well as the nature of the colloidal phenomena, is positive. A clear solution or a whitish or bluish turbidity due to precipitated urates is negative. To prepare the reagent, dissolve with the aid of heat, 173 gm. sodium citrate and 100 gm. anhydrous or 200 gm. crystallized sodium

carbonate in about 700 c.c. of water and filter if necessary. Add slowly and with constant stirring 17.3 gm. of copper sulphate dissolved in 100 c.c. of water. Cool and dilute to 1000 c.c. The reagent keeps indefinitely.

Fermentation Test.—Yeast readily converts dextrose into alcohol and carbon dioxid, and since the latter is a gas, its production may be used as a means of detecting and estimating dextrose. Normal urine gives some gas with yeast this gas often coming from the yeast itself, and the fermentation test must be applied with a comparison or control tube with water free from sugar, yeast from the same source being used in both tubes.

Polarization Test.—Reference is made in the article on carbohydrates to the rotation of the polarized ray, and since, under definite conditions, the degree of rotation is dependent on the amouut of a given substance present, it may be used as a means of detection and determination. In practice, however, there are numerous difficulites. The apparatus is expensive and requires skill in use. Urine, especially in diseased conditions, contains bodies other than sugar which affect polarized light. Levulose, which has left-handed rotation, may be present and render the measurement valueless.

Acetone and Diacetic (Aceto-acetic) Acid.—"A differential diagnosis is sometimes necessary between uremic and diabetic coma, or ketosis may occur for some incidental reason in a nephritic patient. As tests for beta-oxybutyric acid are scarcely practicable, the qualitative reactions for acetone and aceto-acetic (diacetic) acid is used. Quantitative determinations of acetone bodies are not needed for practical purposes even in diabetes." (F. M. Allen.)

Gerhardt's Test for Aceto-acetic Acid.—The simplest method for this is to layer a few c.c. of ferric chloride solution (about 10% strength) under a somewhat larger quantity of urine in a test tube. The pale precipitate of phosphates does not hinder the recognition of the true reaction, which is a color ring of Burgundy red, ranging from a faint tint to almost black. Some crude idea of the degree of the ketonuria is thus obtained, but even approximate quantitative calculations are impossible.

The physician must be on guard that the patient has not been taking drugs (especially salicylates, antipyrin and other coal-tar products) which give false reactions. The color given by the drugs is often atypical, but the distinction is best made by boiling the urine a few minutes and repeating the test after cooling. The false reaction remains, but the aceto-acetic

acid has eben changed into acetone by the heat and the reaction is negative.

Rothera's Test for Acetone.—Place a small amount of the sample in a test-tube and add a large excess of ammonium sulphate crystals; a few drops of fresh 5% sodium nitroprusside solution, and then a few drops of ammonium hydroxide. Through all these steps the tube should be shaken, to maintain a full saturation with ammonium sulphate, and some crystals should still remain in the bottom at the end of the process. A positive reaction consists in a permanganate color, ranging from the palest perceptible tint to almost black. It is necessary to wait almost five minutes to make sure that the maximum intensity of color is developed. Quantitive judgment is based upon the quickness with which the color develops as well as its intensity. For economy when numerous tests are performed it is satisfactory to use only two or three drops of nitroprusside solution with a few drops of urine in a very small test tube and one or two drops of ammonium hydroxide. A fresh nitroprusside solution means one possessing its original red color, which is lost on standing. This change is slower in a dark, cool place, and the solution may be kept for some days. Though this reaction is given by acetone, it is so much more sensitive to aceto-acetic acid, and the latter so predominates over acetone in fresh urine, that the test should properly be regarded as one for aceto-acetic acid *It is valuable as being the most delicate indication of acidosis*, and one purpose in treatment is therefore to keep this reaction continuously negative. As it is sensitive to one part of aceto-acetic acid in 20,000, while ferric chloride reacts only to about one part in 8000 and in urine is often indistinct in its fainter degrees, comparison of different tests is useful. If the nitroprusside reaction is heavy and the ferric chloride negative or faint, there is only slight ketonuria.

Vanillin Test for Acetone. (Leffmann and Trumper).—About 5 c.c. of the urine to be tested are mixed with a strong alcoholic solution of vanillin in a test tube and a fragment of sodium hydroxide dropped in. Acetone is promptly shown by a red ring which deepens rapidly and persists for a long time. The Rothera test color fades out soon and is further found to be unsatisfactory in the presence of albumin (the albumin is thrown out of solution when the urine is saturated with ammonium sulphate) but the vanillin test is still quite satisfactory under this condition.

Acetone is a physiologic as well as a pathologic constituent of urine normally present to the extent of from 3 to 15 mg. per 24 hour output of urine, and greatly increased in starvation, in diabetes and in any

condition in which there is an incomplete combustion of fat as in acidosis.

Indican.—This is a complex body which by oxidation under certain conditions may be converted into indigo. Upon this fact depends its recognition. Jaffé's test for indican is as follows: 10 c.c. of the sample are mixed with an equal volume of strong hydrochloric acid and about 3 c.c. of chloroform. A small amount of solution of sodium hypochlorite is added, drop by drop, shaking after each addition. The mixture is then allowed to stand a few minutes, when the chloroform will collect at the bottom in a layer which will be more or less deeply blue in proportion to the indican present.

Obermayer's Test.—To 5 c.c. of urine add an equal volume of Obermayer's reagent (2 grams of ferric chloride in 1 liter of concentrated hydrochloric acid), and 1 c.c. of chloroform. Cork, and mix thoroughly by repeated inversion of the tube. Allow to stand a short time, and mix again. The reagent oxidizes the ethereal sulphate to indigo blue which is taken up by the chloroform, the intensity of the color being proportional to the amount of ethereal sulphate.

The amount of indoxyl determined in this way is very slight or nil in normal urine; in pathological conditions, however, the chloroform may become blue-black.

If care is used to measure carefully the urine, the reagent and the chloroform, taking the same amounts in every sample tested, one may establish a very satisfactory judgment as to the relative intensity of the "indicanuria." By measuring the blue of the chloroform against a standard color tube a determination of amount of indican is possible.

Ehrlich's Diazo-reaction.—Two solutions are required which should be kept in well-stoppered bottles, preferably in the dark.

Sulphanilic Acid Solution.—1 gram of sulphanilic acid (1–4 diaminobenzenesulphonic acid) is dissolved in water containing 5 c.c. of hydrochloric acid and the solution made up to 100 c.c.

Sodium Nitrite Solution.—0.5 gram sodium nitrite in 100 c.c. of water. To perform the test, 5 c.c. of the sample are mixed with 5 c.c. of the sulphanilic solution and 3 drops of the sodium nitrite solution; 1 c.c. of ammonium hydroxide solution is then poured down the side of the test-tube. Normal urine shows only a yellow or orange, but when the substances which react with the test are present, the liquid becomes red. On shaking the liquid, the red appears also in the froth.

Quantitative Examinations

Esbach's Method.—This depends on the volume of the precipitated albumin measured in a special form of tube called Esbach's albumometer. The manipulation is as follows: The tube is filled to the point U with the sample to be tested, and then to the point R with a liquid prepared by adding 1 gram of pure picric acid and 2 grams of pure citric acid to 100 c.c. of water. If this solution is not clear it should be filtered before being used. After filling the tube as noted, it is closed with a good stopper, shaken several times, and then allowed to stand upright for twenty-four hours. The volume of the precipitate may then be read off on the special scale at the lower part of the tube. The observation must be made at ordinary temperatures and under the conditions noted. Urines very rich in albumin should be diluted with a definite volume of water, and this dilution allowed for. The method is fairly accurate for clinical purposes, especially for successive observations on the same case.

Clinical Quantitative Test (*Folin*).—Pipette 1 c.c. portions of the urine under examination and of 0.1, 0.2, 0.3 and 0.4% albumin solution into a series of similar test tubes graduated at 25 c.c. Make all up to mark with 2% sulphosalicylic acid solution and mix. Let stand for 10 to 15 minutes and compare. A stock albumin solution of approximately 1% strength is made by diluting sheep serum with 7 volumes of 15% sodium chloride solution. This keeps well, and the other standards are made from it by dilution with 15% sodium chloride solution.

Total Acidity (*Folin*).—The urine is titrated with standard sodium hydroxide solution using phenolphthalein as an indicator. Potassium oxalate is added to precipitate the calcium which would otherwise interfere with the end point due to the precipitation of calcium phosphate on neutralization of the urine. The acidity of the urine as determined in this way is not the true acidity, which is dependent upon the concentration of the hydrogen-ion. The results do show a certain parallelism with pH values.

Procedure.—Place 25 c.c. of urine in a 200 c.c. conical flask and add 15–20 grams of finely pulverized potassium oxalate and 1–2 drops of a 1% phenolphthalein solution. Shake the mixture vigorously for 1–2

minutes and titrate it immediately with N/10 NaOH until a faint but unmistakable pink remains permanent on further shaking. Take the burette reading and calculate the acidity of the urine under examination.

CALCULATION.—If a represents the number of cubic centimeters of N/10 NaOH used and b, the volume of urine excreted in 24 hours, the total acidity of the 24 hour specimen will be given by the following equation $25:a:b::x$ (x = acidity of 24 hour urine expressed in c.c. of N/10 NaOH).

Each c.c. of N/10 NaOH contains 0.004 gram of NaOH and this is equivalent to 0.0063 gram oxalic acid. Therefore to express the total acidity of the 24 hour urine specimen in equivalent grams of NaOH, multiply the value of x, as just determined by 0.004.

Ordinarily the acidity of the urine expressed in c.c. N/10 NaOH required to neutralize the 24 hour output varies from 200 to 500 under normal conditions with an average of perhaps 350. It is dependent almost entirely upon the diet, being low on a vegetable (base-forming) diet and high on a diet containing much meat, rice, whole wheat products, fruits containing benzoic acid such as prunes and cranberries, etc. (acid forming foods).

Glucose (*Benedict*).—Benedict's reagent for determination of reducing sugars contains potassium thiocyanate as well as copper sulphate, and in the presence of the former, a white precipitate of cuprous thiocyanate is formed on reduction instead of the usual red precipitate of cuprous oxide. The small amount of potassium ferrocyanide also aids in keeping cuprous oxide in solution. As the precipitate formed is white the loss of all blue tint in the solution, indicating complete reduction of the copper, is readily observed. The alkali is sodium carbonate, which has the advantage over the hydroxide in that there is less danger of destruction of small amounts of sugar. It has also the advantage of being stable. The reagent is as follows:

Copper sulphate, cryst.	18.0 grams
Sodium carbonate cryst.	200.0 "
Sodium (or potassium) citrate	200.0 "
Potassium thiocyanate	125.0 "
Potassium ferrocyanide (5% solution)	5.0 c.c.
Distilled water to make 1000 c.c.	

PROCEDURE.—The sample should be diluted to ten volumes with water (unless the sugar content is known to be very low) and poured into a 50 c.c. burette up to the zero mark. Twenty-five c.c. of the reagent are meas-

ured with a pipette into a porcelain evaporating dish, 10–20 grams of crystallized sodium carbonate (or one-half the weight of the anhydrous salt) are added, together with a small quantity of pumice to prevent bumping and the mixture heated to boiling over a free flame until the carbonate has entirely dissolved. The diluted urine is now run in from the burette, rather rapidly until a chalk-white precipitate forms and the blue color of the mixture begins to lessen perceptibly, after which the solution from the burette must be run in a few drops at a time, until the disappearance of the last trace of blue, which marks the end point. The solution must be kept vigorously boiling throughout the entire titration. If the mixture becomes too concentrated during the process, water may be added from time to time to replace the volume lost by evaporation.

Calculation.—The calculation of the percentage is simple. The 25 c.c. of copper solution are reduced by exactly 50 mg. of glucose. Therefore the volume run out of the burette to effect the reduction contained 50 mg. of the sugar. When the urine is diluted 1:10, as in the usual titration of diabetic urines, the formula for calculating the per cent of the sugar is the following:

$\frac{0.050}{x} \times 1000 =$ per cent in original sample, wherein x is the number of c.c. of the diluted urine required to reduce 25 c.c. of the copper solution. In the use of this method, chloroform must not be present during the titration. If used as a preservative it should be removed by boiling the urine sample and then diluting back to the original volume.

Fermentation Method.—This method consists in the measurement of the volume of carbon dioxide evolved when the glucose of the urine undergoes fermentation with yeast.

Procedure.—Place about 15 c.c. of urine in a mortar, add 1 gram of yeast ($\frac{1}{16}$ of the ordinary cake of compressed yeast) and carefully crush the latter by means of a pestle. Transfer the mixture to a saccharometer, being careful to note that the graduated tube is completely filled with no air bubbles at the top. Allow the apparatus to stand in a warm place (30° C.) for 12 hours and observe the percentage of glucose as indicated by the graduated scale of the instrument. Both the percentage of glucose and the number of c.c. of carbon dioxide are indicated by the graduations on the side of the saccharometer tube. It is well to run a control tube because yeast has the property of splitting off carbon dioxide from the carboxyl group of amino and other aliphatic acids. To determine the total chloride content of urine use the same method and reagents

as given under blood analyses but use ½ c.c. of the sample and calculate for the 24 hour output.

Urease Method for Urea (*Marshall*).—This is a simple clinical method for determining urea, accurate within 2% and rapid.

PROCEDURE.—Two 5 c.c. portions of the urine are measured into flasks of 200–300 c.c. capacity and diluted with distilled water to about 100–125 c.c. One c.c. of a solution of urease (see p. 236) is added to one flask, a few drops of toluene to each and the solution allowed to remain well stoppered at room temperature over night (at least for 5 hours). The fluid in each flask is titrated to a distinct pink color with N/10 HCl using methyl orange as an indicator. A few cubic centimeters of the urease solution used should also be titrated to determine the amount of N/10 HCl required to neutralize 1 c.c.

Calculation.—The amount of HCl required for the contents of the flask containing the urine and urease, less the amount used for 5 c.c. of urine alone and that previously determined for 1 c.c. of urease solution, corresponds to the urea originally present in the sample of urine. Since 1 c.c. of N/10 HCl is equivalent to 3 mg. of urea, the number of c.c. required, multiplied by 0.6 gives the value of urea expressed in grams per liter of urine.

The mean daily excretion of urea normally for adults is from 30 to 35 grams, but varies with protein ingested. As a rule 80 to 90% of the total nitrogen in the urine appears as urea on a high protein diet, but it may go as low as 60% on a low protein diet.

The various determinations of uric acid, creatinine, amino-acid nitrogen, and total nitrogen are seldom made in 24 hour urine specimen for the blood studies of these constituents are of clinical significance.

Urinary Sediments

The sediments which form in urine may be either organized or unorganized. All the forms require the microscope for their satisfactory identification. The organized sediments are principally tube casts, blood or other corpuscles, epithelial cells, and spermatozoids. Many matters entirely foreign to the urine may find their way into it, either by design or accident. A deposit from collodion and iodoform has been mistaken for a urinary sediment. An attempt was made to induce a physician to believe that a piece of brick was a urinary calculus. Those who use the microscope for urinary analysis should familiarize themselves with the

appearance of common objects, such as hair of various kinds, cotton and other fibers, fragments of wood, milk globules, etc.

The unorganized sediments are principally uric acid, urates, phosphates and oxalates. Uric acid is generally in lozenge- or boat-shaped crystals. Urates are indistinctly crystalline; phosphates are generally in distinct prismatic crystals; oxalates in small, regular octahedra.

Urinary Calculi

The common forms of urinary calculi are composed of either uric acid, earthy phosphates or calcium oxalate. Potassium, sodium or calcium urates may also be found, and two bodies—xanthin and cystin—are found quite rarely. The common calculi are generally mixtures of several of the above-mentioned bodies. Calcium oxalate and uric acid often form the nuclei around which other matters deposit. The distinction of the different forms is based principally on the action of heat.

1. A portion of the calculus is heated to redness on a piece of platinum foil. *a*. No residue is left. See 2. *b*. A fixed residue is left. See 3.

2. Apply the murexide test (see below). If this gives a result, the calculus is either uric acid or ammonium urate. If no result occurs, the substance is either xanthin or cystin. See 5.

3. Add a drop of hydrochloric acid to the residue when cold. *a*. It effervesces. The original body was either a urate or oxalate. See 4. *b*. It does not effervesce. The calculus is a phosphate. The result may be confirmed by dissolving a portion of the calculus in hydrochloric acid, and adding solution of ammonium molybdate; a yellow precipitate will be formed.

4. Apply the murexide test to a portion of the original body. If it responds, the body is a urate; if not, an oxalate.

5. The solution of the original body in nitric acid turns yellow on evaporation, and leaves a residue insoluble in potassium carbonate: xanthin. The solution in nitric acid turns dark brown and leaves a residue soluble in ammonium hydroxid: cystin.

Murexide Test.—A small amount of the sample is evaporated on the water-bath with a few drops of slightly diluted nitric acid. The residue, when cold, is moistened with ammonium hydroxide solution. Uric acid and urates give a purple-violet stain. A mixture of a few drops of hydrochloric acid and a small fragment of potassium chlorate can be used instead of nitric acid.

BLOOD

Within a remarkably short time, chemical analysis of blood primarily because of the perfection of colorimetric methods by Folin of Harvard, has won for itself a permanent place in clinical studies and metabolic investigations. The physician now uses blood chemistry not only for prognosis and treatment but most frequently for differential diagnosis. Many of these tests can be carried out by technicians, provided they are supervised by a physician with the requisite laboratory training or by a practical biochemist preferably with a hospital or clinical experience.

Every physician is familiar with the details of collecting blood. There is one point to be emphasized, namely the necessity of using a very sharp needle. The majority of new needles are quite blunt and it is advisable to sharpen them.

The best time for collecting blood is in the morning before breakfast. A few crystals of potassium oxalate will prevent coagulation and a pinch of potassium fluoride may be added as a preservative to the five or ten c.c. of blood. (If the calcium or potassium content of the blood is to be determined sodium citrate must be used instead of potassium oxalate.)

The details of chemical procedure of the numerous tests are available in any laboratory manual, but all these works and even texts on Clinical Diagnosis uniformly fail to mention the valuable information that can be obtained by the inspection of freshly drawn samples of blood, for instance; viscosity, the rapidity of erythrocyte sedimentation (Fahraeus found the rate of sedimentation in pregnant women to reach as high as 40 times that of non-pregnant women). While it cannot be depended on infallibly it is well to record the rate of sedimentation. The relative volume of blood plasma should be observed, especially in anemias and before making a final diagnosis of polycythemia. In leukemias the total white count can be roughly estimated by the thickness of the sedimented film of white corpuscles. It is important to look for abnormal pigments, such as bile pigments in the plasma. Most essential is the observation ot the color of the venous blood for the following reasons:

In all cases of uncomplicated acidosis and in any condition in which the bases in the blood are insufficient to carry the normal amount of carbon dioxide, the venous blood becomes partially arterialized. The extreme arterial color of venous blood can be visualized by the terminal picture of pure diabetic acidosis. It is well known that blood becomes darker as the oxygen is replaced by carbon dioxide and these observations ought not

Results of Chemical Examination of Blood

Condition	Nonprotein nitrogen	Urea nitrogen	Uric acid	"Creatinine"	Sugar	Cholesterol	Chlorides	Diastase	Plasma CO_2
Normal	25–40	10–18	2–3	1–2	90–120	167–255	450–500	8–64	53–77
Exercise, short and violent	.....	.....	.....	.....	Inc.				
Exercise, long and fatiguing	.....	.....	Inc.						
Tropics	.....	.....	.....	.....	Inc.				
Aviation (altitude)	.....	.....	.....	.....	Inc.	.....	.....	.....	Dec.
Furunculosis	.....	.....	.....	.....	Inc.				
Diabetes mellitus, mild	.....	.....	.....	.....	150– 300				
Diabetes mellitus, severe	.....	to 30	4–10	2–4	300–1200	200–800	to 400	Inc.	10–50
Pancreatic disease	.....	.....	.....	.....	Inc.	.....	.....	Inc.	
Arteriosclerosis	.....	.....	Inc.	.....	Inc.	Inc.			
Kidney, passive congestion of	.....	.....	.....	.....	.....	.....	Inc.		
Nephritis, acute	.....	40–200	5–15	2–10	120–180	Inc.	450–600	.....	20–45
Nephritis, interstitial, early	30–50	15–37	3–12	2–4	120–150	.....	450–600		
Nephritis, interstitial, terminal	100–350	60–30	5–27	5–70	120–300	to 300	360–600	Inc.	12–40
Nephritis, parenchymatous (nephrosis)	.....	15–60	2–5	2–4	100–200	to 900	500–600	.....	to 30
Nephritis, chronic, diffuse, severe	.....	to 230	to 10	to 16	to 250	to 412			
Kidney, polycystic, double	.....	to 75	to 5	to 8.5	to 200				
Uraemia	90–350	to 300	.....	4+					
Prostatic obstruction	Inc.	to 30	3– 9	1.5–4	110–160				
Gout	.....	.....	4–10						
Hyperthyroidism	.....	Inc.	.....	.....	Inc.	to 80			
Hypoendocrine conditions	.....	Dec.	.....	.....	60–90	to 1350	Dec.	Dec.	
Pregnancy	Dec.	Dec.	.....	.....	.....	to 500			
Hyperemesis gravidarum	.....	.....	to 5						
Eclampsia	25–45	10–25	4–8	to 2.7	.....	Inc.	Inc.	.....	43–58
Cholelithiasis	.....	.....	.....	.....	.....	130–300			
Acute yellow atrophy of liver	.....	.....	.....	.....	.....	to 87			
Intestinal obstruction, acute	75–170	45–170	Inc.	Inc.					
Fever, acute	.....	Inc.	Inc.	to 4	.....	.....	Dec.		
Pneumonia, severe and late	.....	to 53	to 18	to 3.5	to 180	.....	Dec.	.....	to 33
Anaemia, pernicious	to 108	to 75	to 10	to 3.1	to 300	to 60	to 600	.....	Dec.
Leukaemia	.....	.....	to 10	to 2.5					
Leukaemia, myelogenous	to 110	to 20	to 7.6						
Malignancy, late	Inc.	to 58	to 10	to 3.3	.....	.....	variable	.....	Dec.
Dementia precox, catatonic	.....	6–10	Dec.	.....	Inc.				
Shock	Inc.	Inc.	.....	Inc.	Inc.	.....	.....	.....	Dec.
Oedema	.....	.....	.....	.....	.....	.....	Inc.		
$HgCl_2$ poisoning	to 370	to 300	to 16	to 35	120–200	to 350	to 114	.....	to 25
Plumbism	Inc.	Inc.	Inc.						
Alcoholism	.....	.....	.....	.....	.....	Inc.			
Ether anaesthesia	.....	.....	.....	.....	Inc.	.....	.....	.....	Dec.
Digitalis	.....	.....	.....	.....	.....	.....	Dec.		
Salicylates, antipyrin, quinine	.....	.....	.....	.....	Inc.				
Epinephrin	.....	.....	.....	.....	Inc.				

to be overlooked when sampling venous blood. In short, a physical examination of blood should not be neglected.

With this notice of the advantages of making gross observations of blood and plasma, a synopsis of blood chemistry is presented, beginning with a table taken from E. R. Stitt's "Practical Manual" published by Blakiston of Philadelphia. See p. 230.

An inspection of this table shows the range of values in chronic Nephritis, Uremia, early and severe Diabetes, moderate and severe Acidosis, Gout and many other conditions.

In addition, blood chemistry studies should be made in all pre-operative bladder and prostate conditions. The diagnosis as well as prognosis of toxemias of pregnancy can be better followed by determining the blood chemistry at midterm. In pneumonia correlated cyanosis is observed with venous and arterial unsaturation. Finally, in major fractures when union occurs there is a rise in the inorganic phosphorus content of the blood, but in non-union there is no rise. Blood sugar determinations to control insulin dosage are much used, likewise the determination of plasma chlorides as a guide in many hypertension cases as developed by F. M. Allen.

Under normal conditions the substances found in the blood occur in the proportions given above. The nitrogenous bodies, such as urea, creatinine and uric acid are found in increased amounts, when the kidneys fail to excrete them, and therefore their increase in the blood indicates the degree of kidney dysfunction. Both in acute and chronic interstitial nephritis these products are invariably retained. The urea nitrogen (which normally occurs in the proportion of 12 to 15 milligrams to the 100 c.c. of blood) may be increased to 100 in severe cases and in extreme conditions to as high as 300 milligrams, and the other bodies such as uric acid, urea and creatinine are increased but not proportionately.

The kidneys normally concentrate creatinine about 100 times, the urea about 80 times, but the uric acid only 20 times. Myers, Fine and Lough stated that as the permeability of the kidneys is lowered in renal disease, this becomes evident in the blood, first by a retention of uric acid, later by that of urea, and lastly creatinine, indicating that creatinine is the most readily eliminated of these three nitrogenous waste products, and uric acid the most difficult to eliminate, with urea standing as an intermediate. Folin does not agree with this and points to the retention of all three waste products in advanced cases of nitrogen retention. It is quite true that with almost complete or even partial suppression of renal function as in mercuric chloride (corrosive sublimate) poisoning, there is the

same percentage retention of all three products but such is not the case in typical nephritis. Theoretically, the increase of blood creatinine should be a safer index of the decrease in the permeability of the kidney than the urea, for the reason that creatinine on a meat-free diet is entirely endogenous in origin and its formation and elimination normally very constant.

Urea on the other hand is largely exogenous under normal conditions and its formation is therefore subject to much greater fluctuation. For this reason a lowered nitrogen intake may reduce the work of the kidney in eliminating urea but cannot affect the creatinine to any extent.

Blood sugar (which is normally found in the proportion of 80 to 120 milligrams in 100 c.c. of blood) is increased in amount in diabetes mellitus. In other words, a hyperglucosis or hyperglycemia exists, and findings around 300 milligrams are not unusual and have been known to exceed 500 milligrams.

Very often a marked hyperglycemia exists preceding diabetic coma. This in itself is not so serious, but if it is concomitant with marked increase of acetone-bodies from incomplete fat metabolism with dyspnea without cyanosis, resulting from the excessive withdrawal of bases from the blood, the condition is termed "acidosis" and is quite serious. The diagnosis is best confirmed by a determination of the carbon dioxide combining power of the blood or the hydrogen-ion concentration of the blood plasma. If the patient can co-operate the carbon dioxide content or tension of alveolar air should be taken.

Acidosis.—By this is meant a condition brought about by the excessive withdrawal of alkalies through the formation of fixed acids, or the retention of acids within the body. Recognition of acidosis is very important in diabetes mellitus, severe nephritis, food intoxication and diarrhea with vomiting (particularly in children).

Normally the body is in a state of compensated acidosis and is protected against abnormal conditions as follows:

1. By the proper balance of available carbohydrate in the food against the protein and fat. (Anti-ketogenic *vs* keto-genic.)

2. Selecting foodstuffs not too high in protein because these yield phosphoric and sulphuric acids.

3. Selecting foods containing an excess of inorganic bases over inorganic and organic acids.

4. By an adequate supply of fluids (ketonic acids may be excreted in dilute form).

5. By production of ammonia, which neutralizes acids and conserves sodium, the essential base for carrying carbon dioxide.

6. By the combination of the calcium and magnesium of bone with acids (neutralization).

7. Excretion of buffer salts: acid carbonates and phosphates.

8. Abnormally rapid excretion of carbon dioxide from the lungs.

9. By the use of proteins in the blood or tissues as acids or as bases for combination—to avoid change in reaction.

If one of the above mechanisms is not used during the course of a disease the others may rectify ensuing errors in metabolism, but in severe diabetes some of these are ineffective.

As long as the acid-base equilibrium or hydrogen-ion concentration is normal, there is compensated acidosis. Van Slyke restricts the use of the term acidosis to the condition caused by acid retention sufficient to bring either the acid carbonate or the hydrogen-ion concentration of the blood below normal. A few basic clinical observations on acidosis will be mentioned. It is well to remember that a normal person can hold breath from thirty to forty seconds without an especially deep inspiration, but this period diminishes in proportion to the reduction of the bases in the blood. In acidosis, blood tests are more dependable than alkali tolerance or alveolar carbon dioxide tension tests, because in the latter it is not possible to obtain the cooperation of the semi- or completely comatose patient. In profound diabetic coma, the high renal threshold which is often present (the higher this threshold the more serious is the prognosis) prevents little if any sugar spilling over into the urine, even when the blood sugar concentration is about 300 milligrams, whereas in uremic coma it is common to find trace of sugar in the urine. This makes it difficult to differentiate between diabetic coma and uremic coma unless blood tests are made.

Ordinarily the diagnosis of acidosis can be made or confirmed by any one of the following tests, but if the patient is verging on coma it is necessary to make one of the blood tests, for the other tests (3 and 4) require the cooperation of the patient.

1. Hydrogen-ion concentration of the blood plasma.
2. Alkali reserve of the blood plasma (Van Slyke).
3. Alkali tolerance of the patient.
4. Carbon dioxide tension of the alveolar air.

The meaning of hydrogen-ion concentration and the method of expressing it will be found described on pp. 29–31. The electric methods of determining it involve the use of very costly and intricate apparatus.

Approximations sufficient for most clinical and biologic purposes are obtained by the use of colors which take on changes indicative of certain limits of concentration. For instance, bromthymol blue indicates a range from pH_6 to $pH_{7.6}$ If the color becomes yellow the ion-concentration is pH_6 or below; if the color becomes deep blue the ion-concentration $pH_{7.6}$ or higher. Between these two points the color will range from yellow to blue depending on the pH of the solution.

Practically all the fluids of the body exhibit but slight ion-concentration, so that if expressed or represented by the common fractional methods very cumbersome figures would be needed. Thus, the H-ion concentration of the blood in health is about 0.000,000,04 N, which will be expressed or represented on the standard notation as $pH_{7.39}$. By consulting the table on p. 30 it will be seen that this figure represents a slight alkalinity.

Buffers.—If acid or alkali be added to a solution of a strong base or acid, it will be found that usually the pH is markedly affected. Certain substances, however, when present in the solution, act to modify this usual effect in such manner that the change in pH may be practically inappreciable. Such substances are known as buffers, and they are quite common in biological fluids. These properties of buffered solutions are made use of in the colorimetric method for determining hydrogen-ion concentration. By mixing certain solutions in definite proportions mixtures are prepared of definite pH values. A suitable indicator is then chosen and added to these mixtures and to the unknown. A rough estimate of the pH of the unknown can be obtained by systematically testing it with different indicators, for it shows exactly at what pH the maximum acid or alkaline color may be expected. The exact proportions in which these buffers salts must be mixed to obtain desired pH values can be found in all standard manuals.

The Blood Analysis System of Folin and Wu

Out of the extensive information accumulated on this subject, methods have been chosen which have been found of frequent use and satisfactory. Those described have been used in Jefferson Hospital.

Preparing Protein-free Blood Filtrate.—Measure 5 to 10 c.c. of the sample into a conical flask, add 7 volumes of water by graduate and mix. Add 1 volume of sodium tungstate (10% solution of $Na_2WO_4 2H_2O$) and mix. Add slowly with constant shaking 1 volume of $\frac{2}{3}$ N sulphuric acid. Close the mouth of the flask with a rubber stopper and shake well.

If precipitation is accurately done, on shaking there is a distinct metallic sound and only traces of foam. Allow to stand ten minutes and filter through dry ammonia-free filter paper, discarding the first few drops of the filtrate.

Non-protein Nitrogen.—Put 5 c.c. of the blood filtrate in a dry 25 × 250 mm. pyrex test tube graduated at 35 and 50 c.c. Add 1 c.c. diluted acid-digestion mixture and a dry quartz pebble. Boil vigorously over a microburner until white dense fumes form. Then lower the flame until boiling is just visible, cover mouth of tube with a small funnel and continue heating gently until solution is clear. Remove flame, let cool for 60 to 90 seconds, then add *very cautiously* a few drops of distilled water and dilute to about 20 c.c. Cool to room temperature and dilute to 35 c.c. mark. Then add Nessler's solution to the 50 c.c. mark and mix.

Prepare a standard solution for comparison by placing 6 c.c. of standard nitrogen (0.3 mg. N) in a 100 c.c. volumetric flask, add 2 c.c. diluted acid-digestion mixture and about 50 c.c. water. Then add 30 c.c. Nessler's solution, fill to mark with water and mix. Then compare in colorimeter.

Calculation: $\frac{S}{U} \times 30 =$ mg. nonprotein N per 100 c.c. blood.

To prepare acid-digestion mixture, mix 300 c.c 85% phosphoric acid with 100 c.c. conc. sulphuric (nitrogen free) and 50 c.c. of 5% copper sulphate. Cover well to exclude ammonia. Dilute this acid with an equal volume of water.

To prepare stock Nessler's solution, put 150 gm. KI and 110 gm. iodine in a 500 c.c. round-bottomed flask, add 100 c.c. water and an excess of metallic mercury (about 160 gm.), and shake flask continuously and vigorously for 10 to 15 minutes, or until the dissolved iodine has nearly disappeared. When the red solution is visibly paler, although still red, cool it in running water and continue shaking until the reddish color of the iodine has been replaced by the green of the double iodide. Now separate the solution from the surplus Hg by decantation, and wash with liberal quantities of distilled water. Dilute solution and washings to 2 liters. The working Nessler's reagent is made by adding 75 c.c. of the stock and 75 c.c. distilled water to 350 c.c. 10% NaOH; let stand three days in tall cylinder and use the clear supernatant fluid. To secure the necessary crystal clear solutions for colorimetric comparison in nitrogen determinations, this Nessler's solution must be added after the solution to be tested has been diluted as much as practicable. Add it slowly and during constant twirling.

The stock nitrogen standard solution contains 4.716 gm. $(NH_4)_2SO_4$ per liter. For the working standard (10 c.c. contains 0.5 mg. N), dilute 5 c.c. to 100 c.c. The purest salt obtainable must be used.

To prepare ammonia-free water, add a little dilute sulphuric acid to distilled water and distil. Select such portions of filtrate as show no color reaction with Nessler's solution. The water will absorb NH_3 from the laboratory air, and it is best to distil elsewhere, and to further protect the product by some means as that used for preserving CO_2 free water, using in this case a guard tube of dilute sulphuric acid instead of soda lime.

The principle of the *Urea determination* is to decompose the urea to ammonium carbonate by means of the enzym urease, in the presence of phosphate, the buffer. The ammonia is distilled and collected in weak acid, then Nesslerized and determined colorimetrically.

Put 5 c.c. blood filtrate in a clean, dry pyrex test tube about 200 mm. long and 25 mm. in diameter. A tube that has contained Nessler's solution will probably prevent urease action, and must be cleaned well with nitric before use. Add 2 drops of pyrophosphate mixture (14 gm. sodium pyrophosphate, 2 gm. 85% phosphoric acid and water to make 100 c.c.); 1 c.c. urease solution, and warm in water at 40° C. for ten minutes. Aspirate or distil the ammonia by adding a few c.c. of 10% NaOH or borax and quickly stoppering else, the ammonia will escape. A drop of paraffin oil or 5 or 10 drops of amyl alcohol will prevent foaming. In aerating, do not increase the current of air until after the first few minutes. Allow to aerate for twenty minutes to ensure that all the ammonia has been collected in the receiving tube (containing 2 c.c. of N/20 sulphuric acid). If distillation is used it only takes about seven minutes for nearly all the liquid to pass over.

The standard is prepared by pipetting 6 c.c. of nitrogen standard (0.3 mg. N) into a 100 c.c. volumetric flask and filling two-thirds full with water. To the unknown solution add 2.5 c.c. Nessler's solution, fill to 25 c.c. with water and mix. To the standard add 10 c.c. Nessler's solution, fill to mark and mix. Compare in colorimeter. Calculation: $\frac{S}{U} \times 15 =$ mg. urea nitrogen per 100 c.c. blood.

Urease can be obtained in convenient form from dealers.

It may be prepared as follows: About 3 gm. of permutit are placed in a 200 c.c. flask washed by decantation first with 2% acetic acid, then twice with distilled water. About 100 c.c. of 16% alcohol are

added to the moist mass, 5 gm. of Jack-bean meal, introduced, the mixture shaken for ten minutes and filtered. The filtrate, containing the urease, will keep for about five weeks in the ice box but only about one weeks at room temperature.

Uric Acid (Benedict's Method).—A portion of the blood filtrate is treated directly with arseno-phosphotungstic acid reagent and sodium cyanide. The blue obtained compared in colorimeter with a standard uric acid solution.

Procedure.—Five c.c. of the regular blood filtrate are transferred to a test-tube of 18–20 mm. diameter and 5 c.c. of water added. Five c.c. of standard uric acid solution containing 0.02 mg. of uric acid are also made up to 10 c.c. To both standard and unknown are added from a burette, 4 c.c. of 5% sodium cyanide solution (POISON) containing 2 c.c. of concentrated ammonia per liter. To each tube is then added 1 c.c. of arsenic-phosphoric-tungstic acid reagent. The contents of each tube should be mixed by one inversion immediately after addition of the reagent and placed at once in boiling water, where the tubes should be left for three minutes after immersion of the last tube, but the time elapsing between the immersion of the first and last tubes should not exceed one minute. After the 3 to 4 minute heating, the tubes are removed and placed in a large beaker of cold water for three minutes and read in a colorimeter against the standard as soon as convenient (preferably within 5 minutes after removing from the cold water). It is best not to run more than 4 tubes at a time with one standard.

Uric acid standard solution. The stock solution is made as follows: Dissolve 9 gm. of pure crystallized disodium hydrogen phosphate and 1 gm. crystallized sodium dihydrogen phosphate in 200–300 c.c. of hot water. Filter if not perfectly clear. Make up to about 500 c.c. with hot water and pour this hot or warm (but perfectly clear) solution upon exactly 200 mg. pure uric acid suspended in a few c.c. of water in a liter volumetric flask. Agitate a few minutes until uric acid completely dissolves. Cool, add *exactly* 1.4 c.c. of glacial acetic acid, dilute to mark and mix. Add about 5 c.c. of chloroform to prevent the growth of bacteria or moulds in the solution. Five c.c. of this solution contains exactly 1 mg. of uric acid. This solution will keep for about two months unless in a very warm room.

The dilute standard containing 0.02 mg. uric acid in 5 c.c. is prepared as follows: 10 c.c. of the stock uric acid phosphate solution are measured into a 500 c.c. volumetric flask and the flask is about half filled with dis-

tilled water. Twenty-five c.c. of dilute HCl (1 volume of concentrated acid diluted to 10 volumes with water) are added, and the solution is diluted to 500 c.c. This solution should be prepared fresh every two weeks.

Calculation.—Employing the standard solution containing 0.02 mg. of uric acid and using 5 c.c. of the 1:10 blood filtrate the calculation is as follows:

$$\frac{\text{Reading of Standard (S)}}{\text{Reading of Unknown (U)}} \times 4 = \text{mg. uric acid per 100 c.c. of blood.}$$

Sodium Cyanide.—A 5% solution containing 2 c.c. of concentrated ammonia per liter. Best prepared fresh every two months.

Uric Acid Reagent.—One hundred grams of pure sodium tungstate are placed in a liter flask and dissolved in about 600 c.c. of water. Fifty grams of pure arsenic pentoxide are now added, followed by 25 c.c. of 85% phosphoric acid, and 20 c.c. of concentrated hydrochloric acid. The mixture is boiled for twenty minutes, cooled and diluted to one liter. The reagent keeps indefinitely.

Creatinine.—Put 10 c.c. blood filtrate in a small flask or large test tube and 5 c.c. of the dilute-creatinine-standard in another flask. Add to the standard or control 15 c.c. of water. Add 5 c.c. of freshly prepared alkaline picrate (15 c.c. saturated solution of pure picric acid mixed with 3 c.c. 10% NaOH) to the 10 c.c. of filtrate and 10 c.c. to the standard or control solution. Mix and allow to stand for 7 to 8 minutes. Compare in colorimeter before 15 minutes have elapsed.

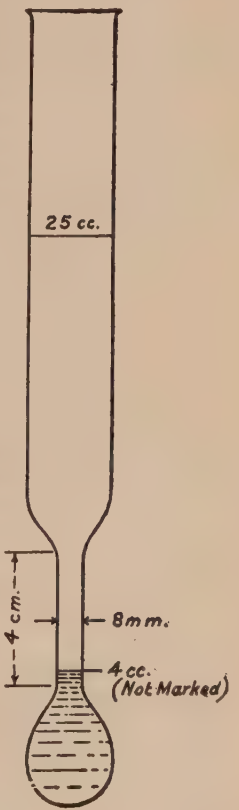
$$\text{Calculation: } \frac{\text{Reading of Standard}}{\text{Reading of Unknown}} \times 1.5 = \text{mg. creatinine per 100 c.c. blood.}$$

Stock creatinine standard is prepared by dissolving 1 gm. creatinine (or 1.6106 gm. creatinine-zinc chloride) in sufficient N/10 HCl to make one liter. Place 6 c.c. of the stock solution in a liter volumetric flask and add 10 c.c. N/1 HCl, dilute to mark with distilled water and mix. Add some toluene to this dilute-creatinine-standard to exclude contaminating bacteria. Both these standards keep indefinitely.

Determination of Sugar.—Principle. The protein-free blood filtrate is heated with alkaline copper solution, using a special tube to prevent reoxidation. The cuprous oxide formed is treated with a molybdate phosphate solution, a blue being obtained which is compared with that of a standard.

Procedure.—Transfer 2 c.c. of the tungstic acid blood filtrate to a blood sugar test tube of the type illustrated (p. 285 *Hawk's* 8th Ed. Fig. 89)

and to two other similar test tubes add 2 c.c. of standard sugar solution containing respectively 0.2 and 0.4 mg. of glucose. To each tube add 2 c.c. of the alkaline copper solution. Transfer the tubes to a boiling water bath and heat for six minutes. Then transfer them to a cold water bath and allow to cool without shaking for a few minutes. Add to each test tube 2 c.c. of the molybdate phosphate solution. The cuprous oxide dissolves rather slowly if the amount is large. When dissolved which generally takes but a few minutes, dilute to the 25 c.c. mark insert a rubber stopper and mix. Be sure to mix well so that the color is evenly distributed. Compare in a colorimeter, using the standard which most nearly matches the unknown.



CALCULATION.

$$\frac{\text{Reading of Standard}}{\text{Reading of Unknown}} \times \frac{\text{mg. of glucose in standard}}{2} =$$

Grams of glucose in 100 c.c. of blood.

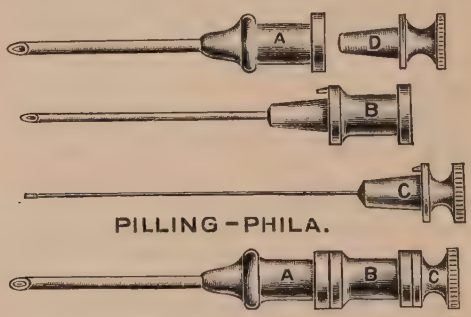
CHLORIDES.—Whitehorn's recent method utilizes the tungstic acid filtrate from either whole blood or plasma, thus determining chlorides of whole blood or plasma. If the plasma sample is taken, it should be immediately centrifuged and separated, or determination is not accurate. The reagents must of course be halogen free.

Put 10 c.c. of blood filtrate and 5 c.c. $AgNO_3$ solution (4.791 gm. per liter: 1 c.c = 1.65 mg. NaCl) in a porcelain dish, stir thoroughly, add about 5 c.c. U.S.P. HNO_3 and let stand five minutes. Add about 0.3 gm. powdered ferric ammonium sulphate, and titrate with NH_4CNS or KCNS solution of which 5 c.c. balances 5 c.c. of $AgNO_3$ solution, to a salmon-red color that persists for at least 15 seconds despite stirring. *Calculation:* 1.65 (5 minus c.c. of KCNS solution required) = mg. chlorides (as NaCl) per 100 c.c. of blood.

In conclusion notice may be made of V. C. Myers' view that the carbon dioxide capacity of blood plasma is probably the most trustworthy single method for determining the degree of acidosis or alkalosis. F. M. Allen of the Psychiatric Institute regards the test as not an infallible index of the acid-base equilibrium of the body. Yandell Henderson's statement is also worthy of attention. A normal person can hold the breath from 30 to 40 seconds without an especially deep inspiration, but the tolerance diminishes in proportion to reduction of the blood alkali.

Annexed is a brief description of a needle which is being used for both tolerance and functional blood tests.

In many functional or tolerance tests (glucose, urea), involving the introduction into and absorption from the alimentary tract of the test



TRUMPER TELESCOPIC NEEDLE

substance, the variable rate of absorption may interfere with the accuracy of the test. This may be avoided by introducing the test substance intravenously.

Blood Volume studies and functional tests which necessitate the repeated venous puncture for blood sampling (vital red, phenoltetrachlorphthalein) are occasionally objectionable to the patient and there may be difficulty in entering the vein at regular stated intervals.

These difficulties may be overcome by the use of the telescopic needle shown herewith. The needle consisting of A, or A and B, is introduced and control sample of blood withdrawn. In children or in patients with very small veins A may be dispensed with. If desired, the flow of blood may be stopped by occluding the lumen with B and C, or C alone if A is not used.

When the test solution is to be introduced, stylette C is withdrawn and reintroduced when the desired quantity of fluid has entered the vein. If B alone has been used, before introducing C the needle is flushed, either by allowing 2 c.c. of blood to flow out or introducing a few c.c. of sterile salt solution. The needle may be held in position by placing a gauze sponge over both ends and fixing with strips of adhesive or narrow bandage. If the patient is restless the arm may be immobilized by a straight splint. Subsequent samples are obtained by withdrawing B and C, the blood flowing out through A.

It is likely that the needle may be allowed to remain in the vein for an hour but thus far it has been used it for periods extending up to 25 minutes during which time three samples of blood have been withdrawn. The danger, if any, lies in the possibility of forcing particles of a blood clot into the vein when stylette C is repeatedly withdrawn and introduced. This matter is now under investigation.

This telescopic needle has been in use in the Jefferson Hospital since September, 1923.

AVOIDING LABORATORY ACCIDENTS

In heating substances in a test-tube, use a holder and direct the tube so that if material is thrown out it will not strike any one. Poisonous and highly irritating substance should not be ground in an open mortar, but covered with muslin or strong paper perforated for the pestle. Inflammable liquids (alcohols, ether, carbon disulphide, benzene and gasolin) must not be distilled or evaporated over an open flame. The only safe way is by an electric heater, and this should have the heating portion enclosed. A light-bulb is a suitable source of heat in small experiments.

FIRST AID

Sodium bicarbonate (acid carbonate) solution (½%) should be used in case of acid burns, followed by copious effusion with water. Burns by strong acid should be at once treated with copious effusion with water. Saturated boric acid solution may also be used. Picric acid solution (7% alcohol containing 7% picric acid) may be applied to burns after thorough cleaning, but severe burns need medical attendance. Tincture of iodine is used for disinfecting small wounds and ferric chloride to check bleeding.

Many small fires can be checked by sand.

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